METALLURGY
OF
LEAD AND ZINC

1936

A. I. M. E.

TN
1
A5
vol. 121
N/C

TRANSACTIONS

OF THE

AMERICAN INSTITUTE OF MINING ~~AND~~ METALLURGICAL and Petroleum ENGINEERS

(INCORPORATED)

Vol. 121

METALLURGY
OF
LEAD AND ZINC

Sponsored by the
ROCKY MOUNTAIN FUND

PAPERS SPECIALLY SOLICITED FOR THIS VOLUME BY THE INSTITUTE'S TECHNICAL COMMITTEE ON REDUCTION AND REFINING OF LEAD AND ZINC

Published by
THE AMERICAN INSTITUTE OF MINING
AND METALLURGICAL ENGINEERS
29 WEST 39TH STREET
NEW YORK, N. Y.
1936

Copyright, 1937, by the
American Institute of Mining and Metallurgical Engineers
(Incorporated)

PRINTED IN THE UNITED STATES OF AMERICA

Second Printing, December, 1937

THE MAPLE PRESS COMPANY, YORK, PA.

COMMITTEE ON ROCKY MOUNTAIN INCOME

Henry Krumb, *Chairman*

Harvey S. Mudd
George Otis Smith

COMMITTEE ON REDUCTION AND REFINING OF LEAD AND ZINC

Carle R. Hayward, *Chairman*
U. C. Tainton, *Vice Chairman*

L. D. Anderson
Frank G. Breyer
George S. Brooks
W. A. Cowan
G. H. Cunningham
E. P. Fleming
Herbert R. Hanley
R P. E. Hermsdorf

G. E. Johnson
Edward F. Kern
J. D. MacKenzie
B. M. O'Harra
George E. Murray
Rudolph Porter
A. L. Queneau
Guy C. Riddell
Blair L. Sackett

Francis P. Sinn
Frank M. Smith
Arthur D. Terrell
H. Y. Walker
Charles M. Warner
Leland E. Wemple
Wallace G. Woolf
Arthur Zentner

A. I. M E. OFFICERS AND DIRECTORS

For the year ending February, 1937

President and Director

John M. Lovejoy, New York, N. Y.

Past Presidents and Directors

Howard N. Eavenson, Pittsburgh, Pa.
Henry A. Buehler, Rolla, Mo.

Vice President, Treasurer and Director

Karl Eilers, New York, N Y.

Vice Presidents and Directors

R. C. Allen, Cleveland, Ohio
Louis S. Cates, New York, N. Y.
Henry Krumb, New York, N. Y.
Paul D. Merica, New York, N. Y.
Wilfred Sykes, Chicago, Ill.

Directors

Erle V. Daveler, New York, N. Y.
Charles B. Murray, Cleveland, Ohio
Brent N. Rickard, El Paso, Texas
G. B. Waterhouse, Cambridge, Mass.
William Wraith, New York, N. Y.
H. T. Hamilton, New York, N. Y.
Wilber Judson, Newgulf, Texas
C. K. Leith, Madison, Wis.
Erskine Ramsay, Birmingham, Ala,
R. M. Roosevelt, New York, N. Y.
Selwyn G. Blaylock, Trail, B. C., Canada
John L. Christie, Bridgeport, Conn.
Eli T. Conner, Scranton, Pa.
William B. Heroy, New York, N. Y.
Frank L. Sizer, San Francisco, Calif.

Secretary

A. B. Parsons, New York, N. Y.

Division Chairmen—Acting as Advisers to the Board

E. H. Dix, Jr. (Institute of Metals), Pittsburgh, Pa.
Hallan N. Marsh (Petroleum), Los Angeles, Calif.
Clyde E. Williams (Iron and Steel), Columbus, Ohio
Eugene McAuliffe (Coal), Omaha, Neb.
W. B. Plank (Education), Easton, Pa.
Oliver Bowles (Industrial Minerals), Washington, D. C.

Staff in New York

Assistant Secretaries
E. H. Robie
Louis Jordan
Assistant Treasurer
H. A. Maloney

Assistants to the Secretary
John T. Breunich
E. J. Kennedy, Jr.
Manager, Mining and Metallurgy
William Handley

PREFACE

During the period since the World War, few papers of major importance have appeared on the production and refining of lead and zinc, although many improvements in technique have been made, which have attracted little attention because they were merely developments of existing practice. Other changes of a more radical nature have also been made, but for business reasons they have been given little publicity.

It seems appropriate, therefore, at this time that the Rocky Mountain Fund Committee of the American Institute of Mining and Metallurgical Engineers should sponsor a volume on Lead and Zinc Metallurgy and that the Committee on Reduction and Refining of Lead and Zinc should attempt to secure papers on various phases of the subject. The response to requests for papers has been gratifying.

Although it is a general policy of the A.I.M.E. to publish only papers that present new or unpublished material, it was the opinion of the committee that the scope should be enlarged in this case so that the volume should represent the present state of the art. Consequently, several papers have been secured describing well-known operations and others presenting material that has recently appeared, at least in part, elsewhere. In addition to this there are papers giving a brief history of lead and zinc metallurgy. We believe the volume justifies this departure from rules.

It is regrettable that one phase of the subject remains untouched. The treatment of secondary material is not yet standardized. Much experimentation is being carried out and few plants care to have their methods discussed. It is hoped that the time is not far distant when some valuable papers will appear in this field.

All members of the committee have cooperated in producing the volume. Some have suggested authors, some have prepared papers, others have read and criticized manuscripts. Special mention should be made of Prof. H. R. Hanley, on whose outline the arrangement of the book is based, of George E. Murray, who helped in many ways, and of Arthur Zentner, who was of special help in connection with the papers on electrolytic zinc.

The committee wishes publicly to thank the authors who have prepared the papers and also the various companies that have authorized the publication of material hitherto kept confidential.

Carle R. Hayward, *Chairman,*
Committee on Reduction and
Refining of Lead and Zinc

Cambridge, Mass.
November 15, 1936

CONTENTS

PAGE
Committee on Rocky Mountain Income 3
Committee on Reduction and Refining of Lead and Zinc 3
A.I.M.E. Officers and Directors 4
Preface. Carle R. Hayward 5

PAPERS

Lead

A Brief History of Blast-furnace Lead Smelting in America. By Arthur S. Dwight 9
Sintering Lead Ores. By H. J. Stehli 38
Blast-furnace Practice at Midvale, Utah. By Galen H. Clevenger 45
Lead Blast-furnace Practice at Trail, B. C. By G. E. Murray 59
Blast-furnace Practice at the Bunker Hill Smelter. By P. C. Feddersen and H. E. Lee 73
Lead Blast-furnace Practice in Missouri. By C. M. Warner 77
Smelting in the Lead Blast Furnace. By G. L. Oldright and Virgil Miller 82
Lead Smelting in the Federal Improved Mechanical Ore Hearth. By L. J. Buck (with discussion) 106
Equilibrium in Lead Smelting. By S. Frederick Ravitz and Kenneth E. Fisher (with discussion) 118
Drosses in Lead Smelters. By C. M. Dice, G. L. Oldright and T. B. Brighton 127
Treating Blast-furnace Drosses. By O. P. Chisholm 160
A Study of Drosses from Lead Blast Furnaces. By G. U. Greene (with discussion) 171
Softening of Lead Bullion. By Arthur E. Hall 194
Debismuthizing Lead with Alkaline Earth Metals, Including Magnesium, and with Antimony. By Jesse O. Betterton and Y. E. Lebedeff 205
Continuous Lead Refining at Port Pirie, South Australia. By G. K. Williams 226
Chlorine Dezincing in Lead Refining. By Jesse O. Betterton 264
Electrolytic Lead Refinery, Betts Process, the Consolidated Mining and Smelting Company of Canada Limited. By P. F. McIntyre 271
Betts Process at Oroya, Peru, S. A. By T. E. Harper, Jr. and Gustave Reinberg 283
Electrolytic Solder. By R. P. E. Hermsdorf and Max Heberlein (with discussion) 289

Fume and Dust Collection

Modern Automatic Baghouses for Collection of Lead-furnace Fumes. By R. L. Hallows and B. M. O'Harra 299
Collection of Lead and Zinc Dusts and Fumes by the Cottrell Process. By Harry V. Welch 304

Zinc

History of the Metallurgy of Zinc. By W. R. Ingalls 339
Sintering Zinc Ores. By H. J. Stehli 374

PAGE
The Warner-Ingalls Zinc-roasting Process. By MUNROE F. WARNER 387
Horizontal Retort Practice of the National Smelting Company, Limited, Avonmouth, England. By T. B. GYLES 418
New Jersey Zinc Company Vertical Retort Process. By E. H. BUNCE AND E. C. HANDWERK 427
Manufacture of Silicon Carbide Retorts. By E. J. BRUDERLIN 441
New Jersey Zinc Company Process for the Refining of Zinc by Redistillation. By W. M. PEIRCE AND R. K. WARING 445
World Survey of Electrolytic Zinc. By ARTHUR ZENTNER 453
The Magdeburg Zinc Works of the Georg von Giesche's Erben Mining Company. By HERMANN BACH, WALTHER HÄNIG, WILLI GEHRHARDT, ERNST THEURICH AND WALTER LANGNER 465
Electrolytic Zinc at Risdon, Tasmania. By W. C. SNOW 482
Electrolytic Zinc Plant of the Sullivan Mining Company. By W. G. WOOLF AND E. R. CRUTCHER 527
Electrolytic Zinc Plant of the Consolidated Mining and Smelting Company of Canada, Limited. By B. A. STIMMEL, W. H. HANNAY AND K. D. MCBEAN 540
The Trollhättan Electrothermic Zinc Process. By W. S. LANDIS (with discussion) 573
St. Joseph Lead Company's Electrothermic Zinc-smelting Process. By GEORGE F. WEATON 599
Intermittent Zinc Distilling from Ore. By W. R. INGALLS 610
Reduction of Zinc Ores by Natural Gas. By H. A. DOERNER 636
Direct-process Zinc Oxide. By E. H. BUNCE AND H. M. HASLAM 678
Treatment of Residues from Electrolysis of Zinc and of Lead-furnace Slags in Ash-fusion Gas Producers. By J. VAN OIRBEEK 693
The Waelz Process. By WILLIAM E. HARRIS 702
Slag Treatment for the Recovery of Lead and Zinc at Trail, British Columbia. By R. R. MCNAUGHTON 721

INDEX 739

A Brief History of Blast-furnace Lead Smelting in America

By Arthur S. Dwight,* Member A.I.M.E.

The author of this historical chapter will perhaps be criticized for limiting his subject to the history of the blast furnace in lead smelting, and especially to the part it played in the great custom ore-smelting business which for three decades or more was the means of opening up vast mineral treasures and practically dominated the mining industry in the Rocky Mountain region of the United States, in Mexico and in Canada.

The men of that era shared the romance and the thrills of mining, and bore their part as pioneers in the building of the great West. The present writer was too young to participate in the first of the three decades mentioned, but immediately thereafter came under the apprenticeship of some of the men who had worked out the early metallurgical problems of the industry, became personally acquainted with most of the others of that group, heard the tales of early experiences, successes and failures, the gossip of the frontier and mining camps, from all of which there remain embedded in his mind clear impressions of the outstanding personalities of that time. That is the background against which the fifty years of intimate contact with the mining and smelting business and his own experiences as metallurgist stand out in his memory, and it is hoped that the gentle reader may understand and approve his desire to rescue from comparative oblivion the fundamentally valuable results accomplished by these fathers of the industry.

It will be the purpose of this chapter first to narrate the general history of the growth of the industry; second, to pay tribute to some of the pioneer metallurgists, and third, to discuss some of the salient points of the metallurgical practice at different periods, to illustrate the technical progress of the art.

The series of eight Annual Reports of Rossiter W. Raymond[1],† U. S. Commissioner of Mining Statistics from 1869 to 1876, contain most of the available information about the early smelting operations in the Rocky Mountain region, and much is in the early volumes of the Transactions of the American Institute of Mining Engineers.

The monograph by S. F. Emmons[2] though not published until 1886, contained an elaborate description of the smelting works operating in 1879. Otto H. Hahn[3] wrote a valuable paper in 1883, on smelting prac-

---

Manuscript received at the office of the Institute Dec. 15, 1936.

* President, Dwight & Lloyd Companies, New York, N. Y.

† References are at the end of the paper.

tice, but after that there was a distinct dearth in the literature of lead smelting until the appearance of Dr. H. O. Hofman's classic work, "The Metallurgy of Lead and the Desilverization of Base Bullion[4]." The value to American metallurgists of this book cannot be overstated. So also should be classed Dr. Hofman's subsequent researches in the thermal properties of silicates and his later book[5], which appeared in 1918. A very concise chronology of the history of lead mining in the United States is to be found in W. R. Ingalls' book[6], published in 1908, together with much interesting metallurgical detail.

Growth of Lead-smelting Industry

The older processes for the production of lead, the English and Carinthian processes, based on the use of the reverberatory furnace, probably enjoyed, with the Scotch hearth, the earliest use by the pioneer miners, as is evidenced by the old ruins that have been described as existing in the Washoe and Washington districts in Nevada, the Patagonian Mountains in Arizona, Little Cottonwood Canyon and Rush Valley, Utah, Cerro Gordo, California and elsewhere. Except the Scotch hearth, these are today obsolete, and the Scotch hearth is limited to the treatment of almost pure galena concentrates, as for instance, in Southeast Missouri, where, supplemented by elaborate means for condensing and recovering the inevitably large amount of lead fumes produced by the hearths, it is commercially successful.

It is not the purpose of this chapter to give further discussion of this branch of lead smelting, important as it is, nor to refer in detail to the small-scale smelting operations in early times at isolated lead mines in the eastern and southern states, as these had no permanent effect on the development of the art.

Rocky Mountain Region

The earliest recorded lead-smelting operations in the Rocky Mountain region were near Helena, Mont., and at Oreana, Nev., on the line of the Central Pacific Railroad in 1866 or 1867. The bullion was cupeled for the silver and the litharge was thrown away.

The completion of the transcontinental Pacific Railways in May, 1869 gave a great impetus to mining and smelting, as it made possible the beginning of more extensive operations, and the shipping of the metallic products to the eastern seaboard, thus putting the lead into direct competition with foreign imports. This started a lead-mining boom.

By reason of the strong affinity of molten lead for the precious metals, and the ease of their subsequent separation, the use of lead as a collecting medium was a feature of the most ancient metallurgical operations, and this principle became the basis of the enormous development which took place in the custom lead-smelting industry on the American continent.

For many years this mode of ore treatment afforded the cheapest outlet for the miner of the precious metals, but its importance began to wane when the supply of dry and siliceous ores diminished and the copper smelters entered the custom-ore field on an increasing scale.

It is generally agreed that Eureka, Nev., was the cradle of modern lead blast-furnace smelting. The first furnace there appears to have been built in the fall of 1869 by Col. G. C. Robbins[1a]. It was a shaft furnace of small dimensions operating on natural draft. In spite of this primitive arrangement it demonstrated the feasibility of smelting the Eureka ores.

This was followed the next year by numerous other furnaces of more efficient though still primitive design and construction, operated by fan blowers, and the lead-smelting business was in for a good start.

Almost simultaneously, a lead-smelting boom started in the Salt Lake Valley of Utah, which seems to have differed in its general practice from that of Eureka. The difference in technique is aptly described by Otto H. Hahn[3], who was one of the earliest of the educated metallurgists to operate in both Nevada and Utah. Therefore, his comparison of the two systems has all the authority of an eyewitness. To quote him:

> The nucleus of the excitement centered about Salt Lake City, whose neighboring mountains were known, from the explorations of the Mormons and the soldiers of General Connor, to teem with lead ores. The comparative poverty of the ores in silver, their siliceous and frequently refractory character, the close competition in their purchases, the bad quality of the fuel and furnace linings, and a good many other things sharpened the intelligence of the Salt Lake Valley smelters more than that of others; and it is to them that we owe the introduction of improvements which led to a more economical handling of the ores. Iron ore and limestone were here used intelligently as fluxing material for the first time. Connellsville coke superseded, at least partially, the miserable charcoal which was made from the light woods of Utah; water jackets replaced the outwalls as well as the costly fire brick lining of the furnaces; dust chambers were erected to save the escaping finest particles of ore; and a number of very complete sampling works were erected, which opened a liberal market to the miner and afforded the smelter an opportunity to select for purchase such ores as suited his wants.
>
> It is true Eureka, Nevada, has been, so to speak, the cradle of the art of smelting in the west; to Ahrents we owe the introduction of the siphon tap, the construction of the first large and successful furnaces, and the reintroduction of the boshes in lead furnaces, but beyond these Eureka does not offer any innovations in the smelting process itself.
>
> The principal reasons for this conservatism (at Eureka) are, first, the docile character of the predominant ore (Ruby Hill) which requires little or no flux to give economically satisfactory results; and secondly, the fact that mines and smelters of the leading companies are managed by the same person, generally a miner or a business man who is reluctant on general principles to attempt improvements of a scientific nature[3].

Hahn generously accords the entire credit to Ahrents for the important progress achieved at Eureka, while the present writer knows from the oral testimony of other witnesses that Hahn himself was entitled to share in the credit for some of the improvements he describes.

Among the Utah plants that made signal advances in good practice, which will be described later, may be mentioned the Winnemuck plant in Bingham Canyon, which began operation in 1872, the Flagstaff smelter in Little Cottonwood Canyon, and the Wahsatch Smelting Works, 7 miles south of Salt Lake City, besides many other small plants.

In the same year the Germania plant was started as a small desilverizing refinery to treat locally some of the argentiferous lead of the district[1d]. In 1875 it went into the ore-smelting business. For many years it was known as one of the outstanding plants in the country, and graduated many highly skilled metallurgists.

The Salt Lake Valley has maintained its importance as a metallurgical center down to the present day. It was surpassed, however, by Colorado from about 1876 to 1886, the years of the enormous output of lead carbonates from the Leadville mines, when its hills fairly bristled with lead stacks. To mention the more important works: The Harrison Reduction Works was built in 1877, the Grant Works in 1878, the Billings and Eilers plant in 1879. The last mentioned was later sold to August R. Meyer and became the Arkansas Valley plant. It is the last of the Colorado smelters to survive the march of time. There were other plants, important in their day, the Elgin, La Plata, Cummings & Finn, and many smaller ones.

On account of high labor and fuel costs the largest plants were moved in the early 80's to Denver and Pueblo, where railroad connections were more favorable for commanding a larger tonnage and variety of profitable ore from widely separated mining districts; a more abundant and reliable labor supply, and cheaper fuel than could be obtained in the mountain camps.

The Pueblo Smelting & Refining Co., the Colorado Smelting Co. (A. Eilers) in Pueblo, the Omaha & Grant Co. in Denver, the Socorro plant (Gustav Billing) in New Mexico, were examples of these migrations; in spite of which Leadville maintained an important place with the Arkansas Valley smelter, the Harrison Reduction Works, the Union smelter, and a few other smaller plants treating a large tonnage.

Additional large plants were built in the "Valley"—the Holden plant, later known as the Globe plant, in Denver, and the Philadelphia smelter, by the Guggenheim interests, in Pueblo.

In the North, the Helena & Livingston smelter, at Wickes, Mont., was moved to East Helena and about 1890 was merged with the Great Falls plant, built by Anton Eilers, and the National refinery in South Chicago, Ill., under the name of the United Smelting & Refining Co., with its principal smelting activities centered at East Helena, the Great Falls plant being finally shut down.

In the South, besides the Socorro (New Mexico) smelter, already mentioned, the El Paso Smelting Works, built by Robert S. Towne and subsequently acquired by the Kansas City S. & R. Co., treated large tonnages of leady and siliceous ores from old Mexico, until a change in the United States import duties on Mexican lead ores interfered with the free entry of some of these ores. This, together with the saving in freight, caused American capital to erect large lead-smelting plants at Monterrey, San Luis Potosi, Velardena, Aguas Calientes and Torreon, though most of the base bullion was brought to the United States for refining.

Nor should we neglect to speak of the plant of the Selby Smelting & Lead Co. at Selby, Calif., which was established in 1866[1a] and has been in practically continuous operation since that time. It has enjoyed almost a monopoly of the ores tributary to the Pacific coast of North and South America, and so has not been a serious competitor of the Rocky Mountain smelters. It refined its own metals and found its principal markets in Asiatic countries.

While it must be admitted that a successful lead-smelting and refining operation was being conducted at Selby three or four years before work began at Eureka, the present writer does not consider that this fact militates against the claim previously made that Eureka was the cradle of the industry. The operations at Selby were apparently not accessible to the public and had very little if any influence on the major developments of the industry in the Rocky Mountain region, while the men of the Eureka and Utah groups established a definite school of metallurgy, their results were published for the benefit of others, and a number of these pioneers continued to be leaders in the business for many years, as will be mentioned later on.

It would seem to be unjust in a discussion of custom smelting in the Rocky Mountain region to neglect to mention the Argo plant of the Boston & Colorado Smelting Co., near Denver, even though it used copper, not lead, as a base, with reverberatory and not blast furnaces. It was probably the first of the copper smelters to go into the custom ore-smelting business on a large scale, and not until many years later did the copper men realize the great possibilities of using copper as a collecting vehicle for the precious metals, and the consequent profits latent in the smelting of custom ores. The company was organized in 1867[7] by N. P. Hill, formerly professor of chemistry in Brown University. A pilot plant was built in 1867 at Black Hawk, but later the works was moved to Argo. The copper matte containing the precious metals was shipped to Swansea, Wales, until 1873, when Richard Pearce, the pioneer metallurgist, succeeded in adapting the Ziervogel process and other improvements, which permitted separating the various metals at home. This plant kept strictly to its own field, but was a vigorous competitor of the lead smelters for siliceous ores.

Movement Eastward

As the chief market for lead and the precious metals was on the eastern seaboard, the movement of the metallic product of the primary smelters was naturally eastward. The precious metals safely locked up in the base bullion could be shipped as commercial lead.

Thus there emerged several industrial groups with plants in the West engaged in primary ore smelting and supplying argentiferous base bullion to their refineries in the East. The St. Louis S. & R. Company's refinery at St. Louis, Mo., was supplied by the output of Socorro and the Harrison Reduction Works at Leadville; the Omaha & Grant Works at Denver had its own refinery at Omaha; the Consolidated Kansas City Smelting & Refining Co., at Argentina, Kans., received bullion from its own plants, the Arkansas Valley smelter at Leadville, and the plant at El Paso, Texas. The smelting plants at East Helena and Great Falls, Mont. had their own refinery at Chicago, Ill. The Guggenheim interests built a large refinery at Perth Amboy, N. J., to handle the products of their plants in Mexico and of their Philadelphia S. & R. Co. plant at Pueblo, Colo. Certain independent refineries treated a considerable share of the bullion output; notably, the Balbach Works at Newark, N. J., the Aurora, Ill., refinery and the Pennsylvania Lead Co., near Pittsburgh, Pa. The Pueblo Smelting & Refining Co. refined its own product.

Economic Factor

A successful lead-smelting enterprise requires as a basis a regular supply of ores and fluxes to furnish the necessary slag-making ingredients. These are essentially silica, iron and lime. There should be a sufficient proportion of lead to "cover" the precious metals. It is manifestly desirable to obtain as large a proportion as possible of these slag-making ingredients in the shape of profitable ores, as any deficiency must be made up by adding barren fluxes to the charge. The ores with less than 10 per cent lead came to be known as "dry" ores, the term being particularly applicable to siliceous ores. The ores carrying a predominance of iron or lime were known as "fluxing ores," and leady ores were even referred to as "lead flux," while ores containing enough iron or lime to flux their own silica were designated "neutral ores."

General mining operations were greatly stimulated by low freight rates to the smelting centers, and the tonnage thus evoked built up the smelting industry to an enormous extent. But as the supplies of the richer lead ores became exhausted, the smelting companies were obliged to economize on their lead. When the lead ores of Colorado and Utah became seriously curtailed and the lead carbonates from Mexico were cut off, lead concentrates from the Coeur d'Alene district of Idaho and from British Columbia took their place, until this supply in turn was partly diverted by the establishment of the local smelting plants at Kellogg, Idaho, Northport, Wash., and Trail, B. C. In course of time a higher price than its commercial value as metal had to be paid for a unit of lead in the ore. This, together with the increasing dependence on barren flux and lime fluxes, tended to throw the entire smelting cost on the siliceous ores. This naturally caused a decline in the smelting business, by rendering low-grade ores unprofitable to mine unless the ore was subjected to concentration, which of course diminished the bulk of material to be smelted and permitted the recovery of metallic values without fluxing and melting large quantities of earthy material. The development of improved methods of grinding and concentration contributed greatly to this result. So also did the slump in the price of silver in 1893. The scrapping of many of the once busy smelting plants gradually ensued. Colorado was more severely hit by these changing economic conditions than was Utah, which has maintained a fairly steady smelting program for many years.

The smelting plants in Colorado, which had long exercised a dominating influence on the industry, were now facing a serious situation; the "handwriting on the wall" was clearly visible in the early 90's. Competition for siliceous ores had become intense. The siliceous gold ores from Cripple Creek, the coppery siliceous silver ores from the Tintic district in Utah, the limey silver ores from Aspen, Colo., were typical of the last remaining tonnages of importance that showed a smelting profit, until finally, in 1894, the smelting companies came together in a "live-and-let-live" agreement and formed the "Colorado Smelters' Clearing House." All the competing companies in that area agreed among themselves to curtail operations and divide the available tonnages in agreed proportions through this central bureau in Denver. Needless to say, this was before the stringent Federal antitrust laws came into being. The plan worked amicably for one year, but it could not save the situation. It did have the merit, however, of bringing the competitors together in closer business acquaintance and reasonable cooperation, so that after a few more years of profitless competition, the principal companies operating in Colorado and Montana, with their eastern refineries, decided in April 1899 to merge their interests into what became the American Smelting & Refining Co. The extensive Guggenheim interests did not at once join the combination, and it was not until about two years later that they came in with Colorado and Mexican plants and their eastern refinery. It was not long until this aggressive group dominated the new company. The policy of the new corporation was to gradually close down and abandon the less favorably situated works and intensify the operations in those remaining.

The more important lead-smelting and refining plants in operation today on the North American continent are shown in Tables 1, 2 and 3.

TABLE 1.—*Potential Smelting Capacity, Silver-lead Plants, North America*[8]

Plants in Operation[a]

Company	Plant	Blast Furnaces, Dec. 31, 1935		Furnaces Actually Operating Sept. 1, 1936	Character of Charge
		Number	Rated Annual Capacity, Tons Charge		
American Smelting & Refining Co.	Durango, Colo.	2	120,000		
	East Helena, Mont.	4	360,000	2	High lead.
	El Paso, Texas	2	240,000	1	High lead
	Leadville, Colo.	2	180,000	2	10 per cent lead
	Murray, Utah	8	584,000	1	High lead
	Selby, Calif.	2	200,000	1	High lead
	Chihuahua, Mexico	8	650,000	4	High lead
	San Luis Potosi, Mexico	2	220,000	2	High lead
Bunker Hill & Sullivan Mining & Concentrating Co.	Kellogg, Idaho	4	450,000	1 or 2	High lead
U. S. Smelting, Refining & Mining Co.	Midvale, Utah	7	530,000	1	High lead
International Smelting & Refining Co.	Tooele, Utah	5	500,000	1	High lead
Consolidated Mining & Smelting Co.	Trail, B. C.	5	700,000		
American Metal Co. (Mexican Division).	Monterrey, N. L.	4	250,000	1	20 per cent lead
	La Fe, Zac.	1	18,000		
	Torreon, Coah.	6	200,000	3	25 per cent lead
		62	5,202,000	21	

[a] Personal communication.

TABLE 2.—*Smelters of Missouri Lead, December* 31, 1935[8]

Company	Plant	Number of Furnaces		Annual Capacity, Tons	
		Blast Furnaces	Hearths	Pig Lead	Concentrates
St. Joseph Lead Co.	Herculaneum, Mo.	3		100,000	150,000
American Smelting & Refining Co.	Federal, Ill.	3	31	160,000	250,000
Amer. Zinc., Lead & Smelting Co.	Granby, Mo.		3	18,000	24,000
Eagle-Picher Mining & Smelting Co.	Galena, Kans.	1	8	55,000	70,000
		7	42	333,000	494,000

TABLE 3.—*Lead Desilverizing Refineries of North America, December* 31, 1935[8]

Company	Plant	Number of Softening Furnaces	Number of Kettles	Annual Capacity for Refined Lead, Tons of 2000 Lb.
American Smelting & Refining Co.	Selby, Calif.	5	1	50,000
	Perth Amboy, N. J.	1	2	90,000
	Omaha, Neb.	4	4	192,000
	Monterrey, Mexico	Harris Proc.	3	180,000
Bunker Hill & Sullivan Mining & Concentrating	Kellogg, Idaho	2	3	125,000
International Smelting & Refining	East Chicago, Ind.	3	8	96,000
St. Joseph Lead Co	Herculaneum, Mo.	1	3	90,000
U. S. Metals Refining Co	Carteret, N. J.	2	5	30,000
U. S. S. Lead Refinery, Inc	East Chicago, Ill.		2	40,000
U. S. Smelting, Refining & Mining Co	Midvale, Utah	2	5	72,000
Consolidated Mining & Smelting Co	Tadanac, B. C.	Betts electrolytic		106,000
American Metal Co., Ltd. (Mexican)	Monterrey, N. L.	4	4	108,000
				1,233,000

Referring to Table 1, it is significant that although only about one-third of the existing lead blast furnaces are in operation today there is being produced a normal tonnage of metallic lead; and it is a fact that the actual smelting rate of a single furnace has been increased to at least double that indicated by the column of rated capacities in the table.

Thus in the 66-year period from about 1870 to the present time, the country has witnessed the growth of a great metallurgical industry that was responsible for an enormous addition to the metallic wealth of the nation, and for the evolution of the art of lead smelting to a high degree of perfection.

To review this dramatic shifting of conditions: the desideratum at the start was the production of metallic lead for itself; later, in what we may call the middle ages, the lead derived a major importance as a vehicle for the collection of the precious metals and became the basis for the enormous expansion of the smelting industry by making possible the cheap beneficiation of all classes of gold and silver ores; still later, as the richer ore deposits were exhausted and new processes came into the field for recovering gold and silver, there was a serious falling off in the ore tonnage available, because of ore shortage, the competition of the copper smelters, and other changes in economic conditions. Consequently there took place a reversion to the earlier practice of carrying heavier lead charges in comparison to the amount of "dry" ores smelted, so that with the greatly increased smelting capacity of a single modern furnace the total tonnage of lead produced has been maintained. That is the situation that prevails in the industry today, thus accounting for the comparatively small number of lead furnaces now in operation.

The Pioneer Metallurgists

The men that may properly be called the fathers of the industry were all men trained in the mining schools of Germany, Freiberg and Clausthal, and these were followed by many younger men, Americans as well as Germans, trained in the same schools. These men exercised the greatest influence in shaping the technical practice at the start and during the first ten or fifteen years. In the 80's, the men trained in our American mining schools began to come into the picture but some of the old-timers maintained their preeminence for many years thereafter. Other men played their part, to be sure, but the ones here mentioned aided the early development of the industry, not only by doing things but by freely sharing their experience with others, and allowing their failures as well as their successes to be published.

Albert Ahrents deserves special mention as one of the pioneer metallurgists of Eureka, for his invention of the siphon lead tap, which furnished the key to the successful adaptation of the blast-furnace principle to lead smelting.

Next should be mentioned Otto H. Hahn, another of the original Eureka group, to whom is attributed the adoption of the rectangular or Rachette type of furnace instead of the round or square section, which permitted the smelting area to be enlarged without increasing the distance between the tuyeres. He is also credited with the adoption of the furnace bosh, a very important improvement. Hahn remained in active and successful practice for a quarter of a century.

As a close third, should be mentioned Anton Eilers, who in the Eureka days was in close touch with the industry in his capacity as Deputy U. S. Mining Commissioner under Rossiter W. Raymond, Commissioner, and who, in that connection, did much by his writings to improve the general smelting practice. Later he became definitely engaged in smelting operations at the Germania Works and the Flagstaff mine at Salt Lake City, and subsequently at Leadville, Pueblo, Great Falls and East Helena. Eilers was responsible for numerous improvements in furnace design and appliances. Perhaps his signal contribution to the art was his development of successful slag types. As previously stated, Eilers' writings were always in favor of a more scientific basis for the industry. He urged better accounting methods and better control of operations. In 1875 he published statistics[9] to show the high metal losses in some of the best of the Nevada and Utah smelting plants, and made a most urgent plea for more capacious dust chambers, the utilization of the values in the matte, and the establishment of "complete chemical laboratories which are so far, I am sorry to say, nowhere to be found." He estimated that in consequence of these wasteful practices even with the extraordinarily rich ores then being treated only two or three plants in Utah and Nevada out of forty or fifty then operating had paid a reasonable interest on the capital invested, and many had gone completely bankrupt. He retained his connection with the smelting business to the end of his life. During his more active years his plants were considered models of efficiency and good management.

The name of August Raht should be included in this pioneer group. Famous for his work in the old Horn Silver mine, Utah, he later operated in Montana, at the Helena & Livingston Works, the Philadelphia smelter at Pueblo, and the other plants of the Guggenheim Brothers in Mexico, and Perth Amboy. He was remarkably clear-headed and direct, and became noted as a "trouble man," reorganizing the practice in plants suffering from metallurgical troubles.

Von Liebnau was one of the pioneer metallurgists at Eureka; Alfred Wartenweiler, Ellsworth Daggett and Brueckner in Utah.

As the industry grew in magnitude, many highly trained young men became connected with the calling, and the steady increase in efficiency, technical excellence and low smelting costs bear witness to their genius and zeal. The pages of our technical literature contain the record of their achievements. The standards established for lead smelting in the United States have become the standards the world over.

The Blast Furnace

In tracing the lines along which progress has been made in the art of lead smelting, we must consider first the appliance that has the most prominent place in the picture and that is of major importance in lead smelting—the blast furnace. Essentially a vertical, hollow shaft with means for supplying an upward current of air to support combustion within a descending column of ore and fuel, this simple, almost crude mechanical device is capable of a remarkable degree of efficiency and fuel economy under intelligent handling and coordination of conditions. To the experienced metallurgist his furnaces have an almost human interest. With proper mechanical and chemical conditions once established, absolute uniformity of composition and correct distribution of the charge and, in short, uniformity of all the major conditions, will ensure fast-running, clean and uniform slags, low dust and fume loss and prolonged campaigns.

The term "muscular metallurgy" aptly describes the early smelting practice. The furnaces were small and freeze-ups more than common;

little was understood about slags; too much fuel was used, which made "iron sows" in the crucible, overfire and high metal losses. Viewed in the light of modern practice, early conditions were distinctly haphazard and terribly wasteful. The crowbar and sledge hammer furnished the cure-all, and was the final resource of the harassed furnaceman.

From the original furnace in use at Eureka, Nev., in 1870[1a] to a modern furnace there was a gradual growth in the size of the shaft, as illustrated by the following examples, characteristic of successive periods:

After the historic though impractical "draft furnace" already described as built by Colonel Robbins near Eureka in 1869, the first really respectable type was that adopted in 1870 by the young metallurgists trained in Germany. This may be considered the primordial American lead-smelting blast furnace, and as such deserves a brief description. The structure was of stone with a lining of slabs of sandstone. The area at the tuyere level was 3 ft. square, the height from tuyeres to the single charge door was 12 ft., and the shaft was surmounted by a chimney with no dust chamber. There were three tuyeres, water-cooled. The crucible was 2 ft. deep below tuyere level, with an open breast for slag overflow and arranged for tapping lead, matte and speiss at the bottom, the latter two by-products going over the dump with the slag. Eight to nine tons of carbonate ore was smelted in 24 hr., averaging 45 per cent lead, $75 in silver and $15 in gold. The fuel was charcoal, supposed to be 25 per cent of the ore, but seems often to have run up to 50 per cent. The blast at first was supplied by fan blowers; later by small Roots blowers. No flux was added and the slag averaged about 30 per cent SiO_2, 50 per cent FeO, 7 per cent CaO and over 8 per cent PbO. About 3 per cent speiss was made.

Chemical analysis played practically no part in the smelter routine. There must have been almost continuous overfire, so that with no dust chambers, rich matte and speiss thrown over the dump, it is easy to understand the statement in Raymond's Report for 1870:

> When the furnaces are properly managed the loss of lead will probably not exceed 20 per cent. At present, however, it is larger, owing to several reasons, and very largely to the frequent use of crowbars about the hearth, whereby a great deal of lead is mixed with the slag.

This was indeed the age of "muscular metallurgy."

One recorded test of metal losses showed 30 per cent of the silver and 40 per cent of the lead unaccounted for, and this can easily be believed under the conditions described, but the accuracy of the test is open to doubt, owing to the haphazard methods of operating. The actual losses might have been less, but probably were not. The point that interests the metallurgists of today is that such a condition should have been accepted as inevitable. Independent of these frightful metal losses, the cost of smelting a ton of ore is said to have been about $20.

Approach to the Modern Furnace

Of course, such primitive methods could not be tolerated very long, and the enterprising young metallurgists at Eureka Consolidated brought to bear some of their knowledge of German practice by building a larger furnace of the octagonal Piltz type, as used at Freiberg, Germany. This furnace[1a] had an equivalent diameter of 5 ft. at tuyere level, seven water-cooled tuyeres, a charge column of 12 ft., in a flaring shaft that widened to a diameter of 6½ ft. at the charge-floor level. The slag overflowed at an open breast, and the lead, speiss and matte were tapped from the crucible bottom at intervals. This "large furnace" was hailed as a wonderful improvement. Next the Rachette, or rectangular, furnace was tried and found to possess distinct advantages. It became the prototype of the modern American lead blast furnace. Whatever hesitation there may have developed in adopting it was probably due to the difficulty of reaching the rear of the crucible with the steel furnace bar, but the more skillful metallurgists favored it.

Raymond's report mentions the siphon tap as having been "lately" added to the Piltz furnace at Eureka by Albert Ahrents, "the metallurgist of the Eureka Consolidated Company, which increases considerably the already astonishing results obtained with this shaft furnace." This improvement by Ahrents can justly be claimed as the most important improvement ever made to the lead blast furnace. It permitted the maintaining of a bath of hot molten lead under the smelting laboratory region of the furnace, thus contributing enormously to the maintenance of proper slag temperatures and the prevention of iron sows, the bugbear of the early metallurgists, which we now recognize as due principally to the excessive amount of fuel charged, aggravated by the periodic draining of the crucible.

Next in importance to the siphon tap, the water jacket should be mentioned. The credit for this improvement is lost in the maze of controversy. Water-cooled tuyeres had been used in the stone and brick furnace walls of the early Eureka furnaces and a so-called "hydrocycle," a round water-cooled furnace, was built at the Richmond Consolidated at Eureka about 1871 but did not last long. It was not until 1874 that we find mention by Eilers[1f,10] of the introduction of the water-cooled furnace jackets. T. A. Rickard[7] states that the first water-jacketed furnace in Colorado was built near Silverton in 1875 by John A. Porter, Freiberg graduate, and previously assayer at Eureka. Porter was for many subsequent years a successful operator.

Cast-iron water jackets were the fashion for two decades, but for the modern large-capacity furnace steel jackets are preferred. After the adoption of the water jackets the water-cooled tuyere gave place to a simple sheet-iron tuyere nozzle, connected with the "bustle-pipe" nipples by canvas bags, which acted as safety valves in case of blower stoppage and back-pressure of explosive furnace gases. But this arrangement involved considerable loss of air, especially as higher blast pressures were adopted, so the automatic box tuyere designed by A. Eilers came into vogue. This had a self-closing valve to protect against back-pressure, and thus permitted airtight ducts from blower to furnace and resulted in considerable saving of power. Other similar safety devices have been used. The usual diameter of the tuyere nozzle is 4 inches.

The water jackets rested on the brickwork of the crucible and extended upward 4 to 6 ft., including the "bosh." Above the jackets the shaft was of firebrick to the level of the charge floor. As blast pressures increased, a second tier of water jackets was often added. Modern practice seems to favor making the entire shaft from the crucible top to the charge floor of steel water jackets, but some good metallurgists adhere to the single tier of jackets, and a brick shaft to conserve the heat. Much store was set by the metallurgists in the 80's on the interior lines of the furnace, and each one built his furnace to suit himself. There was general agreement as to the rectangular shape of the hearth (Rachette type) with a width varying from 36 to 50 in., depending somewhat on the blast pressure employed. In the 80's the usual length of the hearth was about 8 ft. but modern furnaces have been as long as 16 ft. The only limit to the length is the ability to provide a perfectly even distribution of the charge. Emmons says of the Leadville furnaces in 1879 that an area of 3 ft. by 7 ft. 9 in. was the largest then existing.

Iles[11] describes the furnace that he considers ideal for the conditions existing in Colorado about 1900 as one with an area at the tuyeres 42 in. wide by 140 in. long, equal to 40.80 sq. ft., a 10-in. bosh, 16-ft. ore column, horizontal area of shaft at charge floor 100 sq. ft. compared to 69 sq. ft. at top of boshes. This general type has remained standard to the present time, though modified in width and length to meet the demand for larger tonnages, and with improvements in structural details. Some modern examples will be adequately set forth in the other papers in this volume.

The bosh has a double function. It tends to confine the smelting zone to a reasonable distance above the level of the maximum heat intensity immediately in front of the tuyeres, by allowing the ascending gases to expand and cool somewhat before rising into the zone of reduction above. The bosh also acts as a bearing surface against which the ore charge can temporarily arch itself and gradually feed down into the smelting zone as the charge is melted away below it. The height of the bosh section varied from 3 to 4 ft. and the slope varied from 2¼ to 4¼ in. per foot of height. Too flat a bosh is not desirable, as it lets the charge hang up unduly and furnishes a platform on which furnace accretion is apt to build up. A 10-in. bosh found the most favor.

Above the bosh the walls of the shaft preferably flare outward, so that the area of the "throat" of the furnace at the level of the charge floor will bear a ratio to the area at the tuyere level as much as 2½ to 1. This upward enlargement of the furnace shaft has fully demonstrated its utility. The ascending gases are slowed up, thus giving them a chance to more thoroughly permeate the descending ore charge, and by reduced velocity to carry over a minimum of dust into the flues, while the gradual expansion of the gases cools them and tends to avoid a premature ignition of the coke and consequent overfire and accompanying metal losses. The height of effective charge column varies from 14 to 21 ft. above the tuyere level.

The furnace gases may be taken off through flues immediately below the charge floor, or by hoods or superstructures of metal or brickwork above the charge floor and connected with the dust flues, baghouse or Cottrell fume-recovery plant. As most modern furnaces are fed by mechanical means, the first named, or "open top," type is preferred.

Reduction

"Reduction" is a general term used by lead metallurgists to express a condition in a furnace that is the resultant of a number of factors, the visible measures of which are the percentage of lead in the slag and matte, the amount of matte fall, and sometimes, if there is arsenic in the ores, by the formation of speiss. All of these results are dependent upon the amount of iron reduced, so the term "reduction" is not inept. The chief controlling factors are: percentage of fuel and its character, the volume and pressure of the blast, height of the ore column, its mechanical disposition in the shaft, and its permeability to the gases. Other conditions being equal, a loose charge will allow more sulphur and arsenic to be oxidized and make less matte-fall; but unless fuel and air are coordinated, it may cause overfire with higher lead assays of slag and matte, but still it may be made to yield fast and clean running. A tight charge usually means slower running, more iron reduced, lower lead in slag and matte, larger matte fall, and probably speiss. The happy medium, of course, lies between the two extremes, but the skillful metallurgist can at will effect remarkable changes in the chemical analysis of his slag and matte and in throwing his iron from one to the other, by modifying the balance between some of these purely mechanical factors. These principles were not as well understood a generation ago as they are today, and there was a good deal of incorrect reasoning and much unnecessary metallurgical grief. The making of speiss is a sign of too strong reduction and there is no necessity nowadays for making any under ordinary smelting conditions.

In considering the factors controlling reduction, the influence of the physical condition of the charge column as affected by the manner of feeding will be later explained. The question of fuel is, of prime importance of course.

Fuels

In the pioneer days in Nevada, for instance, charcoal, which could be obtained in the neighboring hills, was the logical fuel. Immense quantities were used, from 25 to 50 per cent of the smelting charge. It is no wonder that iron sows in the crucible became the chief bugbear of the metallurgist. The readily ignited charcoal commenced burning high up in the shaft, caused overfire and high metal losses. It is easy to understand the reasoning that continued to keep the fuel percentage high. The small furnaces were prone to "freeze up" for one cause or another, probably refractory slag or improper feeding, so what could be a more natural order than "Give her more fuel, boys." This usually increased the trouble, but was nevertheless the standard remedy.

The first record we have of the substitution of coke for charcoal is given by Ellsworth Daggett[14], who tells how Alfred Wartenweiler, in charge of the Winnemuck smelter in Bingham Canyon, Utah, in 1872 began the use of Connellsville coke. His tests convinced him that coke was twice as effective as charcoal, while the costs per ton of fuel were then about equal. However, considerably higher metal losses ensued, "due to much higher temperatures when coke was employed." That reasoning, however, was incorrect. We now know that the efficiency of coke to charcoal in the blast furnace is about 4 to 1, so that after allowing 2 to 1 as the ratio in substituting one fuel for the other the percentage of coke on the charge was double what it should have been, and made trouble.

The Utah smelters abandoned the use of charcoal long before the Colorado operators. Emmons stated[2] that the fuel consumption of the Leadville smelters averaged 22 to 24 per cent, while in Salt Lake Valley 14 to 17 per cent was then the rule. The former used mixed coke and charcoal; the latter presumably coke alone. He says: "Charcoal of good quality will smelt more charges in the same time than coke, but coke will make cleaner slags and less flue dust than charcoal. A mixture will be more advantageous economically in many localities than either alone." This reflects the opinion of that time. The long accepted myth that more fuel was needed at higher altitudes is open to serious question, at least in the opinion of the present writer. The Colorado smelters continued to use the mixed fuel until about 1892. The abandonment of charcoal was a great improvement metallurgically and economically.

In present practice it is customary to figure the amount of coke needed in terms of fixed carbon, and the usual percentage is 9 to 12 per cent of the furnace charge (ore plus fluxes). Metallic iron, usually in the form of scrap iron, has been in general use in lead smelting. If in solid form so as to carry down to the tuyeres unchanged, it may be figured as displacing the coke pound for pound, but tin cans and iron turnings cannot be so figured.

The Blast

In the small furnaces of early days the blast was supplied by small Roots blowers and the pressures employed were low. The Baker blower gained favor in the 80's and was largely used in Leadville, Pueblo and Denver until the Roots company built a sturdier machine than their older models with less air slippage than the Bakers, and so again gained the supremacy. The Connersville blower became a serious rival of the Roots and offered some structural advantages. The East Helena plant adopted electrically driven piston blowers, which certainly possess theoretical and probably actual economies. All these blowing engines of increased capacity and power are rendered necessary by the increasing size and height of the enlarged furnaces.

It was customary up to about 1900 to have all the blowers driven from a common line shaft and deliver into a common blast pipe from which the individual furnaces took their supply. This arrangement worked well if all the furnaces offered the same resistance, but if any one of the battery tightened up, and consequently needed more pressure, it failed to get its share. The later practice of providing an adequate blower for each furnace resulted in increasing tonnages.

Dust and Fume

Flue dust and metallic fume have already been mentioned as dangerous avenues for metal losses. The really sinful disregard for the waste of nature's resources which characterized the first years of the Eureka operations gave place to efforts to cut down the fume and dust loss. The Richmond Consolidated Co. built a system of sheet-iron dust flues, 8 ft. wide by 8 ft. high with hopper bottom, 800 ft. long, leading to a wooden stack 40 ft. high located on a hillside 200 ft. above the furnaces. The metal loss in 1873 before the flues were installed was reported by the company to be 20 per cent, while in 1874 after the flue system was completed the loss had been reduced to 12 per cent, of which a large proportion was accounted for in the speiss, which was thrown over the dump.

In the same year the Eureka Consolidated built a similar flue system 800 ft. long. Presumably other plants took the hint and adopted this simple economical measure.

From this time on until the turn of the century the prevailing practice favored large brick chambers with zigzag turns to expand and slow up the flue gases, and allow the dust particles to settle. Then it came to be recognized that cooling and friction were very important aids. The system of hanging in the flue groups of parallel iron plates in line with the travel of the gases, as used by Freudenberg at Ems, Germany, or the

Rösing system of suspended wires was widely used and found to be very efficacious. If the gases have been previously cooled, friction with the plates settles the dust rapidly.

A great advance was made when the practice was adopted in the 90's of filtering the furnace gases through cotton or wool bags. According to W. R. Ingalls[12] the use of filter bags goes back to 1850. In 1851 Wetherill, at the New Jersey Zinc Co., used bags to collect the zinc oxide in connection with his process. Bartlett used a baghouse to collect the zinc-lead pigment at his works at Joplin, Mo. The first recorded attempt to use the baghouse for lead furnaces is mentioned by Emmons[2] as having been tried at the Grant Works in Leadville about 1879, but only experimentally. Malvern W. Iles and associates at the Globe Smelting & Refining Co., Denver, deserve the credit for working out the problem of the large baghouse for lead smelting. It is standard practice today, though with numerous variations.

For many years the smelters enjoyed comparative freedom from complaint and lawsuits on account of smoke nuisance. In a scattered community, usually interested in mining, the occasional whiff of sulphur smoke was all in the day's work, and the killing of the vegetation was a matter of indifference, but as the neighboring population increased, and especially as farmers found that "smoke-farming" could be made more profitable than truck farming, the smelters began to have their troubles. A long series of lawsuits with volumes of expert testimony, resulted in court decisions that established a series of definite codes regulating the maximum percentage of free SO_2 that can be released in the furnace gases. These factors vary with atmospheric conditions, humidity, temperature, and so forth.

This situation naturally put severe limitations on the smelting companies and called for numerous expedients to meet local situations. A policy frequently adopted was to buy up all the farms in the vicinity and resell them with a smoke clause in the deed. Some even established farms to prove to the doubting farmers in the neighborhood the advantages of smelter smoke as an insecticide.

The last word in means for recovering dust and fume from furnace gases is the direct-current electrostatic process devised by Dr. Frederick G. Cottrell about 1908. It was previously known that an alternating electric current would cause particles suspended in a fairly quiescent atmosphere to agglomerate and settle, but in a rapidly moving gas stream the action is too slow to be effective. Cottrell secured the desired result by using a high-potential intermittent direct current (20,000 to 30,000 volts). The current is discharged from electrodes of various forms, wires, rods, chains or plates and causes the particles of dust or fume to be deposited on metallic plates as collecting electrodes on the opposite side of the gas stream. Many structural and electrical difficulties had to be overcome, but the final result is a brilliant success, and reflects great credit on the distinguished inventor and those operating metallurgists who assisted in working out the problems. As a Cottrell plant is much cheaper to construct than a baghouse of equal capacity, the former is now generally chosen as additional capacity when needed. Thus many plants have both systems in operation.

Handling Materials and Products

On account of lack of space no attempt will be made to record in detail the gradual improvements that took place in the handling of materials and products in the period under consideration. It must suffice to say that the smelters generally took advantage of the mechanical appliances available in the market for cheapening their operating costs, such as mechanical devices for unloading ore, crushing, conveying, sampling, bedding, roasting and delivery to the furnace. The flue-dust bugbear found a temporary solution in briquetting but this was never entirely satisfactory. It is now so simple to include flue dust, baghouse and Cottrell fume in the charge to the sintering machines that handling any kind of fine material has ceased to be a problem. Automatic ore sampling largely replaced the old method of split shovel and sampling by quartering. Mechanical feeding will be discussed more in detail further on.

As the furnaces increased in size and output, the small hand-trundled slag pot, with overflow matte pot, gave way to the large brick-lined matte settlers and large-capacity slag cars, drawn by locomotives. With sufficient settler capacity, the practice of tapping the fluid interior of the slag pots and resmelting the shells, which prevailed for many years, was found to be of doubtful value, especially as the function of slag in opening up the blast-furnace charge was taken by sintered ore. The large reverberatory slag-settling furnaces were successful in cleaning the slags when conditions were favorable, but with high-zinc slags, or with furnace irregularities, much trouble resulted from dross and mush and the general operations of the plant were impeded.

Instead of molding the bullion from the siphon tap directly into final bars, as was the custom for a long time, the best modern practice is to transport it in molten form or to resmelt the rough bars in a large drossing kettle, to be there drossed, poled, and dip samples taken as the clean lead is molded into shipping bars. Such a sample is far more correct than the old-time punch sample.

Mechanical Feeding

It is now recognized that the manner in which the charge is fed to the furnace can exercise an enormous influence on the mechanical and even the chemical reactions in the furnace, introducing disastrous irregularities if carelessly done, and capable of modifying the heat balance or even nullifying the effect of otherwise well established factors.

Some experienced metallurgists still cling to the virtues of hand feeding, but the advantages of a well designed mechanical feeding device, intelligently adapted to the special conditions of a given plant, have been amply demonstrated by the experience of the past thirty years or more.

The first attempts in this direction consisted in adopting the bell and hopper feeder of the iron-furnace practice. O. H. Hahn[3], writing in 1882, refers in a general way to unsuccessful experiments with bell and hopper feeder at Freiberg, Germany, which failed "because the heat crept up in the furnace and produced overfire." This was first tried in this country by A. F. Schneider about 1888, on a lead furnace of circular section at the works of the St. Louis Smelting & Refining Co. Afterwards the same device was applied to a round furnace treating refinery products at the Guggenheim refinery at Perth Amboy, N. J. There is reason to believe that at both places the tightly closed top caused the chimney draft to draw up the heat in the furnace, thereby causing a tendency to overfire. Aside from this disadvantage, however, there seems no good reason why the bell and hopper feeder might not give a proper disposition of the charge if properly placed in a round furnace of limited size.

But when it came to feeding a rectangular furnace with two bell and hopper feeders, as was done in the first furnaces installed in the Guggenheim plant at Aguas Calientes, Mexico, the first principles of correct feeding were violated and the metallurgical results were not merely unfortunate, they were devastating. This episode furnishes such a unique and dramatic example of "what not to do" that it seems appropriate to give it mention in a history of lead smelting, however brief. Hiram Hixon[13], who chanced to be in charge of the Aguas Calientes plant when these furnaces were started up, about December, 1895, tells a weird tale of his experience. With a charge containing 14 per cent lead, there was absolutely no bullion produced, only slag and matte. Bars of bullion fed into the furnace entirely disappeared. All efforts proved useless until the bell and hopper device was removed and the furnaces were fed by hand with open top. Then lead began to flow normally. Hixon says that:

> after careful sampling and weighing all products, and giving credit for the lead in the slag, which was all high in silver and lead, it was found that 63 per cent of the lead end 23 per cent of the silver was unaccounted for.

Hixon attributed this extraordinary degree of volatilization of lead to two things:

> First that a lead furnace closed on top will soon show overfire, and the lead will be wholly or partially lost as volatilized fume; second, that increasing the distance

between tuyere level and feed floor beyond the proper height of the smelting column has the same effect as closing the top of the furnace. It assists in volatilizing lead by preventing the cold air which is drawn in above the charge from cooling the top layers of the charge.

The present writer gives some slight weight to the first of Hixon's reasons, but none to his second. There are numerous lead furnaces with closed tops operating successfully today with higher charge columns than Hixon describes. Taking all the facts into consideration, it is quite apparent that the unfortunate experiences at Aguas Calientes were due in major part to the incorrect placing of the coarse and fine portions of the charge in the furnace.

The first successful mechanical feed was that installed on the furnaces of the Pueblo Smelting & Refining Co. in 1895, known, after the designer, as the Williams system[14]. It was the prototype of the systems subsequently adopted by many other plants. It consisted of a 3-ton rectangular charge car with a W-shaped bottom nearly the size of the upper cross section of the furnace, moved sideways up to the feeder floor on an inclined trestle by a tail rope from a pit on the level of the ore bins, where the weighed ingredients were dumped into the car by the charge wheelers. The furnace top was closed by doors, which were opened when the charge car was about to discharge. Three angle bars extended across the furnace shaft to act as deflectors to break up the falling stream of ore, while the shape of the car bottom tended to throw the charge against the furnace walls, the correct disposition. The plan was correct in principle and it worked successfully.

The next attempt at mechanical feeding was made about 1899 by Hiram Hixon[14], then superintendent of the East Helena plant of the United Smelting & Refining Co., later taken over by the American Smelting & Refining Co. The battery of furnaces had been arranged for hand feeding through narrow slots in the level charge floor. Hixon adopted the Pueblo idea of the large charge car but with a square drop bottom, drawn up by a steel cable from a loading pit and capable of discharging its load through the charge slots by dropping the hinged bottom halves. The results were disappointing, the furnaces developed overfire, and after numerous trials under varied conditions, the device was allowed to stand idle, and the furnaces were fed by hand.

In 1900 the present writer had occasion to visit the plant in a consulting capacity[15]. He induced Hixon to start up the mechanical feed for observation. Sure enough, the furnaces promptly got hot on top, but a careful study showed the cause. The fines of the charge, which sifted down, first made a pile along the center of the furnace under the feeding slot, from which the coarse lumps rolled off against the walls, just the reverse of what proper feeding required. A long A-shaped spreader was hastily built of wood, plated with sheet iron and hung longitudinally in the furnace shaft under the feeding slot, in such a position as to throw the falling ore stream against the furnace walls, banking up the fines there and allowing the major part of the coarser lumps to roll toward the center, thus establishing the ideal disposition. The furnaces picked up in speed, the slag and matte assayed lower in lead, and in proof that there was never any more overfire, it may be stated that the original wooden spreaders remained in use for months exposed to the furnace gases without being even charred, until they were replaced by permanent spreaders made of steel.

This spreader, with occasional slight modification, is now employed as the basis for most of the systems of mechanical feeding of lead furnaces. The underlying principles involved in correct feeding were set forth in a paper by the present writer[14], and the correctness of the conclusions there enunciated has stood the test of 35 years experience in many plants.

Another feeding device, which is now in use in several large plants, is known as the Australian feeder. It resembles in principle a furnace top that was used on small blast furnaces in Germany in 1858, called the Darby feeder. The type now employed follows the lines of a feeder designed by Philip S. Morse at the works of the Sulphide Corporation, Boolaroo, Australia, in 1902. It was later installed by him at the Selby Works, California, and has been adopted at Monterrey and Torreon, Mexico. A similar construction was used by the present writer on one of the furnaces of the Cia. Metalurgica Mexicana, San Luis Potosi, Mexico, in 1902, the furnace making an unusually long and successful campaign. It consists of a rectangular smoke-pipe concentric with the rectangle of the upper shaft, leaving a marginal slot along the sides, and in some cases the ends, through which the charge is fed. The fines hug the walls and the lumps tend to roll to the center, giving the ideal distribution for equalizing the upward flow of the furnace gases in the shaft.

Slags

The slags made in lead blast-furnace smelting are assumed to be composed chiefly of mixtures of ferrous and calcic silicates, with other bases replacing in part the iron and lime. There exists an enormous amount of empirical data on slags, much of which is contradictory, with too much generalization based on special local conditions, coupled frequently with bad observation. However, out of the experience of the last 60 years there have emerged certain type slag analyses which have proved their worth, and which are generally accepted by the careful metallurgist as empirical guides. They cover a wide range of variation of the iron and lime constituents, thus permitting a slag to be chosen to best meet the commercial conditions of the local ore supply, relative cost of fluxes, etc.

In the happy-go-lucky days of muscular metallurgy at Eureka, Nev., in the 70's, when the unusually favorable, self-fluxing ores of Ruby Hill were being treated, anyone who would have talked of the necessity of chemical analysis, in order to make a slag conforming to a scientific formula, would have been regarded as a very unpractical person. Probably many a perfectly good smelting enterprise with a rich lead property to back it went bankrupt because it tried to imitate the Eureka rule-of-thumb practice and smelt a refractory ore without fluxes. In chapter X of Raymond's Report for 1872 there is an excellent article by Eilers and Hahn jointly, in which the fundamental principles of lead smelting are set forth, including the theory of fluxing refractory ores. As these Government reports had a wide circulation, it is probable that this article had an immediate effect in improving the practice in this respect, and certainly this was true in the Salt Lake Valley smelters, as stated by Hahn[3].

A few years after the article by Eilers and Hahn was written, Eilers had embarked actively in the smelting business. While operating at the Germania Works, and later at the Flagstaff mine, he traced back the analysis of some of his best slags to the corresponding chemical formulas, and settled upon certain of them as types[3]. Based upon the ratios of CaO to FeO, he called them "quarter," "half," "three-quarter" and "one to one." He figured the other bases present as replacing the main bases at their relative molecular value, MnO as replacing FeO, and MgO and BaO replacing CaO, then allowing room for other foreign bases (RO) such as ZnO and Al_2O_3, but not altering the SiO_2 percentage except empirically as the behavior of the furnace and the appearance of the slag required it.

August Raht, at the Horn silver mine, and Albert F. Schneider, with his assistant, T. S. Austin, at the Germania smelter worked out in 1880 a formula for the one to one slag, practically similar to the Eilers type[16], and treated the "foreign bases" in the same manner.

These type slags were not universally accepted by the metallurgists in the 80's and 90's but, as a matter of fact, all were following more or less the same line, conforming to certain approved analyses, and correcting the slag empirically by actual observation. For, after all, the ultimate test of a correct slag was its physical behavior and characteristics, its freedom from lead and silver, and its favorable influence on the furnace.

In 1902, T. S. Austin and William Allen Smith, at the El Paso plant of the American Smelting & Refining Co., developed an entirely new and most significant theory of slags, which has worked out in practice with signal success. The theory assumes that a slag is practically a chemical salt, or a combination of base and acid, and that a correct slag is one in which the silica is exactly neutralized by the bases. Primarily, the general proportions or type of the slag must be chosen in view of the commercial conditions. Its formula can then be deduced from the average of a great many analyses of good slags. Following this plan, they selected four principal types, which happened to correspond fairly closely with the Eilers types; one to one, three-quarters, one-half and two-fifths, but with an important difference, in that all of these El Paso type slags presented the same ratio between the acid and bases, which the Eilers types did not do.

The neutrality factors, together with a convenient table of the Austin-Smith slag types, have been published in H. O. Hofman's Metallurgy of Lead, 1918 edition, page 311.

In their calculations, the foreign bases, MnO, MgO, BaO, etc., were to be given their atomic value in replacing the principal bases, but Al_2O_3, ZnS and ZnO were considered as inert, not combining with silica, but dissolved or suspended in the neutral slag magma.* Fluorspar was also considered as similarly inert, the Ca not to be counted with the CaO. Therefore, instead of following the Eilers method of keeping the SiO_2 unchanged and lowering the FeO plus CaO to make place for the foreign bases, the Austin-Smith method was to reduce the three main slag ingredients sufficiently to accommodate the foreign bases, but keeping the relationship between the SiO_2, FeO and CaO equivalents unchanged. The neutrality of a given slag can be tested by multiplying the FeO and CaO equivalents by the corresponding saturation factors and comparing the total with the actual silica. This theory offers a very satisfactory and practical working basis for the lead metallurgist.

However, the last word has not been said on the subject of the composition of slags in general. It must be admitted that the microscopic studies of solidified slags seems to throw doubt on the role of the particular silicates assumed to take part in the slag types we have been discussing. Dr. William Campbell[17] in explaining certain silicate diagrams makes the following sweeping statement:

> The above diagram shows the absurdity of figuring MgO as CaO in calculating blast furnace slags. Furthermore to give chemical formulae to any slags, ferrous or non-ferrous is quite as absurd, because they are all mechanical mixtures when examined under the microscope.

Coming from such an eminent authority as Dr. Campbell, this statement is something of a bombshell. It can at least be said, however, for the slag formulas and types, that they have served a useful practical purpose as working theories in the development of present lead-smelting practice, and until the practical metallurgist learns to run his furnaces on slag diagrams, freezing curves, and eutectics, he will probably cling to his old slag types.

---

* Private notes.

Preparation of the Ore

A very important adjunct to the smelting operation has been the preliminary preparation of the ore and especially the elimination of the sulphur by roasting. Wartenweiler, at Winnemuck plant, Utah, in 1873 or 1874, appears to have been the first to roast and resmelt matte[1f,10]. For this he used heap roasting, and later stalls. He was then able to cut down his use of barren iron flux, which costs up to $18 per ton. He then started roasting some sulphide ores, both in heaps and in a double hearth reverberatory 9 ft. wide and 15 and 17 ft. long, respectively, using lignite for fuel.

After this demonstration of the advantages of roasting the crude ore and the matte, the practice became general, and the long-hearth, hand-rabbled reverberatory roaster became the standard practice and was in general use until about 1908, when it was replaced by the blast-roasting processes. In the meantime, however, various types of mechanical roasters came into use, displacing to some extent the hand roasters, and even after the introduction of blast roasting continuing their usefulness for preroasting the sulphide ores and mattes.

It was the copper smelters that did the most to develop the mechanical roaster. Beginning with the O'Hara, which simply dragged the rabbles by chains along the hearth of a former hand-rabbled furnace, the Brown-O'Hara protected the chains by placing them in corridors alongside the hearth. Then came the Brown-Horseshoe, the Keller, the Ropp, the Pearce, and a long line of hyphenated patented furnaces, as one inventor made a small improvement on a previous one. Of these, the Brown-Horseshoe, the Pearce and the Ropp were the ones of the flat hearth type most used by the lead smelters. The Godfrey, a circular revolving hearth with stationary rabbles, was used in connection with the Huntington-Heberlein blast-roasting process, and the Herreshoff and Wedge multi-shelf furnaces have been much used for preroasting matte. It is not necessary to describe these various types, as they are adequately pictured in the standard works on lead metallurgy.

It cannot, however, be said that the lead metallurgist was ever truly in love with the mechanical roaster of any type. The difficulties caused by the low melting point of the lead compounds, gumming up the rabbles and building up the hearth whenever the temperature got out of control, caused constant shutdowns and worries.

The Brueckner cylinders were free from these troubles and had quite a vogue, but they as well as the hand roasters and most of the mechanical roasters have given way to blast-roasting processes.

Of the blast-roasting processes, the first to be adopted on a large scale was the Huntington-Heberlein method, which was originated in Italy in the 90's and covered by U. S. patents issued in 1897 and 1898.

It consisted of five operations: preparing of crushed ore, mixing of lead ore and limestone, rough roasting in a reverberatory furnace, moistening the rough-roasted mixture, igniting at the bottom, forcing air through it in an iron pot (updraft), discharging and breaking the large cake of agglomerated charge so formed. The theory upon which the original patents were based—that the lime had an important chemical effect essential to the process—was a fallacy. It has since been demonstrated conclusively that the useful function of the lime was to isolate the sulphide particles from one another and prevent their melting together, and this function could be served by other refractory particles, such as silica. The invention, however, was a great contribution to the art of lead smelting, ranking in importance, in the opinion of this writer, with Ahrents' invention of the siphon tap. The process found extensive application in Australia and the patent rights were purchased by the Guggenheim interests for use in this country. Large plants were installed in the first years of the present century and it was generally agreed that some of the hitherto serious problems of roasting and smelting of lead ores were satisfactorily solved. The old troubles of reverberatory roasting were forgotten and the coarse fragments of Huntington and Heberlein agglomerate made beautiful material for the blast furnaces.

One of the disadvantages was the cost of breaking up the big 10-ton cakes of hot, dense agglomerate, and this, together with the great cloud of suffocating leady dust that followed the dumping of every pot, was unhealthful for the workmen and caused an unusually large amount of lead sickness[18].

The pioneer work in blast roasting in this country by James W. Neill[19] should not be overlooked. In 1883, at Mine La Motte, Mo., with a crude hearth improvised from an old Scotch-hearth furnace, he roasted some nickeliferous pyrite with an updraft air blast. Later, in 1889, at the Harrison Reduction Works, Leadville, he converted an idle blast furnace into an updraft roasting apparatus by arranging a horizontal grate above the tuyeres and leaving out the front jackets for a working door. On this he roasted a considerable tonnage of lead sulphides.

Taking the hint from this device, John Williams, at the neighboring Arkansas Valley plant, built a more elaborate roasting plant on this principle, with a battery of grates, which operated for some time but was finally abandoned.

In 1894, Neill, operating in Bingham Canyon, Utah, built a small updraft grate furnace to treat some sulphide copper ore from a leased property, but a larger plant was built by him for the Yampa smelter, in Bingham Canyon and treated successfully several hundred tons. This furnace was sold in 1902 to the Boston & Montana smelter at Great Falls, Mont., where it was operated under the direction of R. L. Lloyd and roasted about two thousand tons of copper concentrates. Lloyd was later associated with the present writer, then general manager at Cananea, Mexico. There was a large tonnage of fine sulphide copper ores and concentrates, with only blast furnaces to smelt them. Recognizing the possibilities of improving on the blast-roasting method of Neill with which Lloyd had been familiar in Montana, a series of experiments were commenced in 1905 on the Cananea ores with improved apparatus. They found that with an updraft blast, the product while desulphurized was very irregular in physical character and contained a large proportion of fines. Careful study of the procedure when using the shallow grates and also deep updraft pots brought the conclusion that the fines resulted principally from the agitation of the particles by the air blast, and that if the particles could be held in quiescence in contact with one another along the surface of exit of the gases they could be sintered into a coherent cake. Various expedients were tried to effect this, but the simplest and the one that finally did the trick was to reverse the air blast. This was the basic idea of the resulting Dwight & Lloyd downdraft process of roasting and sintering[20].

A layer 4 to 6 in. thick of moistened fine ore of uniform density placed on the grate, ignited on its upper surface and subjected to a downward-moving air current, generally by suction, would roast and sinter the charge to a coherent porous cake, easily broken to convenient size for blast-furnace charging and peculiarly susceptible to easy and efficient reduction by the furnace gases. This product came to be known as "D. & L. sinter." The ignition being on the upper surface made it possible to devise continuous operating machines for carrying on the process under highly efficient and economical conditions. The crushed material to be sintered is stored in bins equipped with automatic feeders, which can be set to deliver continuously definite proportions of ingredients to a conveyor belt moving in tandem with the sintering machines, thus making the entire system continuous. It is now standard practice in most lead smelters, and is so adequately described in the textbooks and technical literature that no detailed account will be given here. It is now used throughout the world. The process has found more general application in smelting lead, zinc, nickel and iron than in smelting copper, for which it was originally worked out, as in copper smelting the reverberatory furnace remains supreme.

It may not be amiss, in a historical discussion to resuscitate the results of a study of the relative efficiencies (Table 4) of the different roasting processes used in lead smelting, which the present writer made some years ago and which was first published in 1911[21].

The hearth area for the purposes of this comparison was taken as the area of the layer undergoing treatment, which in the Dwight-Lloyd sintering mechanism is the area of the suction box. The reader is referred to the original article for further details.

The facility with which zinc sulphide was broken up in the steady blast of fresh air on the sintering machine, compared to the sulphur-laden gases of the ordinary hearth roasting furnace, furnished an opportunity to solve one serious problem confronting the lead smelters in the early 1900's due to the increasing tonnages of very zincky lead concentrates, and especially flotation concentrates which came up for treatment. The usual preliminary roasting on hearth furnaces followed by the sintering process did not relieve the blast furnaces of the "zinc-mush plague." An improved technique was worked out at the East Helena plant of the American Smelting & Refining Co. about 1912 by Guy C. Riddell, then superintendent, whereby a properly adjusted and prepared ore charge was passed twice over the D. & L. machine, giving it what has come to be known as "double roasting." This procedure has been of great benefit to the lead smelters in taking care of blast-furnace charges high in lead and containing much zinc.

TABLE 4.—*Efficiency Factors of Ore Roasting*

	Efficiency Factor, Ore Treated per Day per Sq. Ft. Hearth Area, Lb.	Character of Product for Blast-furnace Smelting
I. Roast heaps and stalls	5 to 20	Good
II. Reverberatory roasters:		
1. Hand roaster	24 to 35	Fair
2. Mechanically stirred:		
Average conditions	33 to 75	Too fine
Special conditions	150	Too fine
3. Revolving cylinder	128	Too fine
III. Blast roasting in pots, average	500 to 900	Excellent
	600	Excellent
IV. Blast roasting in thin layers, Dwight-Lloyd system:		
1. Intermittent downdraft pans	1000 to 2000	Excellent
2. Continuous sintering machine	2200 to 3000	Ideal

Aside from the purely mechanical advantages of the D. & L. process, which are attested by numerous authorities, the remarkable diminution in the terrible results of lead poisoning of smelter employees, which for many years was the curse of the industry, should be mentioned. To quote from the U. S. Government Report previously referred to:

> Not only has this process (D. & L.) cheapened and improved the work in every metallurgical sense, but the conditions of operating can be made far superior from the hygienic standpoint to those of any other similar process. This comes from the fact that a positive suction at all points of the active operations can be made to draw all gas, fume or smoke from the machine and not permit it to escape and poison the workmen[18].

References

1. R. W. Raymond: Statistics of Mines and Mining in the States and Territories West of the Rocky Mountains. Government Printing Office, Washington.
    - *a.* For the year 1870 (1871).
    - *b.* For the year 1871 (1872).
    - *c.* For the year 1872 (1873).
    - *d.* For the year 1873 (1874).
    - *e.* For the year 1874 (1875).
    - *f.* For the year 1875 (1877).
2. S. F. Emmons: Geology and Mining Industry of Leadville, Colorado. Government Printing office. Washington, 1886.
3. O. H. Hahn: Smelting of Argentiferous Lead Ores in the Far West. U. S. Geol. Survey, *Mineral Resources of the U. S.* (1883) 324.
4. H. O. Hofman: The Metallurgy of Lead and the Desilverization of Base Bullion.
5. H. O. Hofman: The Metallurgy of Lead. 1918.
6. W. R. Ingalls: Lead and Zinc in the United States. New York, 1908. Hill Publishing Co.
7. T. A. Rickard: History of American Mining. A.I.M.E. Series, 1932.
8. W. R. Ingalls: Year Book American Bureau of Metal Statistics (1935).
9. A. Eilers: Avoidable Waste in American Lead Smelting Works. *Trans.* A.I.M.E. (1874–75) **3,** 98.
10. A. Eilers: Progress of the Silver-lead Metallurgy of the West during 1874. *Trans.* A.I.M.E. (1874–75) **3,** 307.
11. M. W. Iles: Lead Smelting. New York, 1902. John Wiley & Sons.
12. W. R. Ingalls: *Eng. & Min. Jnl.* (1905).
13. H. Hixon: Lead and Copper Smelting. New York, 1897.
14. A. S. Dwight: The Mechanical Feeding of Silver-lead Blast Furnaces. *Trans.* A.I.M.E. (1901) **32,** 353.
15. G. C. Riddell in Liddell's Handbook of Nonferrous Metallurgy. New York, 1926. McGraw-Hill Book Co.
16. A. F. Schneider: High Percentage of Lime in Lead Shaft-furnace Slags. *Trans.* A.I.M.E. (1883) **11,** 56.
17. W. Campbell in Liddell's Handbook of Nonferrous Metallurgy.
18. A. Hamilton: Lead Poisoning in the Smelting and Refining of Lead. U. S. Dept. of Labor. Washington, 1914.
19. J. W. Neill: Recent Progress in Blast Roasting. *Trans.* A.I.M.E. (1910) **41,** 915
20. A. S. Dwight: *Mineral Industry* (1907) **16,** 380.
21. A. S. Dwight: Efficiency in Ore Roasting. School of Mines *Quarterly* (1911) **33.** No. 1.

Sintering Lead Ores

By H. J. Stehli,* Member A.I.M.E.

Probably the earliest sinter from lead ore was made in the product sinter boxes attached to some hand reverberatory roasters. The ore was drawn from the roaster bed when dead roasted, and then by laborious effort fritted together by rabbling at a high temperature in the sinter box. This was not a true sinter, but was a great improvement over the dusty dead-roasted fine ores.

The Huntington-Heberlein pots were the first real advance in the art, and produced some real sinter. They required that the sulphides be preroasted to 5 or 6 per cent sulphur, and the long cycle of operating and deep bed of material used in the pots fostered the formation of densely fused material and fines. This necessitated crushing of the densely fused cake and returning to the next charge large amounts of fines screened out.

The Huntington-Heberlein pots made comparatively high lead losses because the deep bed and high internal temperature together favored the volatilization of lead. Lime (CaO) was added to the charges, and this addition constituted the patented feature of the Huntington-Heberlein process. Its sole function we now know was to act as an isolator of the sulphide particles, and any other substance—for instance, iron oxide—of equal fineness performed the same function.

The Savelsberg process used limestone instead of burned lime, and in this there was a definite advantage. The converting of $CaCO_3$ to CaO is a highly endothermic reaction, so the lime acted not only as an isolator of sulphide particles but absorbed excess heat and to some extent prevented premature fusion of the sulphides.

The Carmichael-Bradford process used gypsum instead of limestone, and had the disadvantage of adding more sulphur to a charge from which it was desired to eliminate sulphur. Here again the gypsum served only as an infusible isolator of sulphide particles.

The first Dwight-Lloyd apparatus to sinter lead ores commercially was installed at Perth Amboy in 1907. The fact that lime in any form was necessary to sintering was quickly disproved by making excellent sinter from Bunker Hill and Sullivan table concentrates, silica sand and iron oxide only.

Manuscript received at the office of the Institute Sept. 17, 1936.

* Metallurgical Engineer, New York, N. Y.

Some of the lead sulphide ores, and more especially lead matte, proved troublesome to sinter until it was discovered that the ¼-in. size to which they were crushed for the hand roasters was entirely unsuitable for the sintering machine. Finer grinding solved this difficulty.

The Dwight-Lloyd machine was successful in making a highly desirable blast-furnace product from a large variety of lead-bearing materials. Sintering was rapidly adopted by lead smelters in the United States, Canada and Mexico, and subsequently all over the world for sintering lead ores, because of the superiority of the product and the simplicity and low cost of the operation.

Soon hand and mechanically rabbled reverberatory roasters, Brueckner roasting cylinders and other similar devices were completely discarded by lead smelters, and a little later most of the pot sintering plants were abandoned.

Many of the so-called lead ores and concentrates of the early days, except those from Missouri and Wisconsin, were lead ores only by courtesy. They sometimes contained more zinc than lead, and usually enough zinc to make plenty of trouble in the blast furnaces. Today all of these ores are treated by selective flotation, so that now the lead-sintering plant gets reasonably zinc-free ores and concentrates, and the formerly troublesome zinc now goes to zinc-sintering plants, where it is very successfully desulphurized and sintered.

Difficulty with High Sulphur

The difficulty in the earlier days was that the ores contained lead sulphides with a low fusion point and zinc sulphides with a very high ignition point, as well as slag-forming substances capable of forming slags of low fusion point. If the sintering were conducted at a low temperature, the lead sulphides would roast until the heat developed reached the fusion point of the lead sulphides or the fusion point of the slags. The zinc sulphides would remain almost unaltered, because even if temperatures were reached at which the zinc would desulphurize readily, the whole charge was so covered with a slagged coating that the air could not reach the zinc sulphide particles. As a matter of fact, unless sulphide concentrates containing much zinc were given a long preroasting treatment to break up the zinc sulphides, they sintered poorly.

However, even in smelters treating lead charges containing no zinc, as at Alton, Ill., and Herculaneum, Mo., a raw concentrates charge when mixed with necessary fluxes contained 8 to 9 per cent sulphur. It was not possible to get this down by sintering much below 3 or 3.5 per cent sulphur by one-pass sintering, therefore matte in considerable quantities was produced in the furnace, and this had to be ground and re-added to the sintering charges, where it made trouble usually unless ground very fine. The whole trouble came from the fact that even with a low ignition and careful operation, if a charge had more than about 6 per cent sulphur, temperatures would be developed as the sintering progressed that would finally fuse the remaining lead sulphide into matte—whereupon roasting ceased.

In other words, a charge contained so many heat units that if an attempt was made to burn them up in short periods in sintering, excessive temperatures were generated. This action could be counteracted to some extent by taking steps to absorb as much heat as possible in one way or another, run thinner beds, add limestone where the slag composition permitted, or iron flux in the form of limonite or carbonate if available, or other substances containing combined water or carbon dioxide, which would absorb much heat in being driven off and so hold down the temperature in the sinter bed.

Water absorbs excess heat in evaporating, therefore should be used in as large a proportion as possible. An ideal condition existed when a plant had all of its sulphides in the finest possible condition, minus 200-mesh flotation concentrates, and its iron in the form of fine limonite. If the SiO_2 was contained in the sulphide concentrates, and this charge was properly mixed and conditioned by pelleting, 8 to 9 per cent initial sulphur could be reduced to 1 or 1.5 per cent in the sinter.

However, such ideal conditions seldom occurred, and even when found could not have much effect because there was no proper mixing apparatus for pelleting the charge. For most ores, limitations made 4 per cent S in the sinter the low average possible, and this was not enough to avoid the formation of matte in the blast furnace; therefore all plants searched for a way to get lower sulphurs in the sinter.

Double Sintering

It was found that in preroasting ores, it was not necessary to do any very thorough roasting to get good results in the subsequent sintering; in fact, provided sulphides were given a "singe"—if I may use that word—so that the surface of the particles was roasted, the tendency to fuse prematurely was stopped. As many works had no preroast furnaces, they began to try to find substitutes, and the Dwight-Lloyd machine itself was the one readily available device. As a roaster on straight high sulphides, it was not very satisfactory, because, as already explained, violent action due to high sulphurs caused quick blinding of the bed by matte and stopping of the roasting action.

The next thought was, since the trouble was that at a certain point in sintering a charge the cumulative heat was too much, why not sinter up to this point, then stop, cool down the sinter, crush it, and then mix it with water again and start over a second time? This would give a preroast and would put all the material into a granular condition (like popcorn), as that is the effect of a quick preroast, especially if after the preroast it is suddenly chilled by wetting down.

When this was tried, the product sintered well on the second sintering if a certain minimum of sulphur was present. This was easily attained by the addition of small amounts of raw sulphides if the first roast was too low. As a matter of fact, a small amount of raw sulphides is a great help to the ignition, particularly if it can be fed out on the top of the charge. Other things being equal, the top layer of a bed can stand much higher sulphurs than the bottom, because the cooling effect of the air is greater on the top and the bottom is subjected to cumulative heating from above. If a segregating hopper is used, the sulphide fines are almost sure to be mostly on top.

This double sintering worked out so satisfactorily that soon it was almost universally adopted, and today a lead furnace makes no matte, or only the minimum amount that may be necessary to keep silver low in the slags.

Another variation of this method less used, but quite as good in many ways and having one great advantage in small plants—that of requiring only one sintering machine—consists in constantly returning to the charge an amount of finely crushed sinter—about 50 per cent. The result of this is a lower initial sulphur and the forming of an open and granular charge, so that upon sintering a low-sulphur sintered product is made.

The disadvantages of this method are that good, solid sinter must be crushed to furnish the material for mixing with and diluting the sulphur of incoming raw concentrates, whereas in double sintering the first sinter needs practically no crushing, as it is usually, if sintered at all, very friable. The advantage is that only one machine or set of machines is required—that the feeding, conveying and mixing are much simplified from that required for double sintering, and installation costs are therefore lower, even when the sinter-crushing apparatus is figured in. A distinct advantage lies in the ability to change the procedure to suit changes in ore supply or charges.

It is simply a matter of crushing and returning more or less of the sinter to suit conditions. For double sintering, the number of preroasting and finish-sintering machines required must be decided before the plant is erected. If this number is miscalculated, either there will not be enough of one or the other to permit of first roasting and finish-sintering a given number of tons in the same time, and even if this is determined correctly, a change in ore supply later on may throw this balance out. One peculiar effect of the double roast made on two machines is the formation of metallic lead. This does not occur by the sinter-returns method. The explanation is that in the double sintering, little or no sinter is formed in the first roast. Hence such PbO as is formed is not combined with SiO_2 as in returns sintering; hence, when sintered the second time, there is a chance for the reaction between PbS and PbO to form metallic lead.

Frequently Cottrell fume, baghouse fume, and other materials carrying lead oxide, are added to the charge for the second roast, and whenever this is done, metallic lead may be looked for, often to such an extent as to cause trouble in removing it from the windboxes. With baghouse fume, this difficulty can to a considerable extent be eliminated by adding the baghouse dust unburned to the charge instead of burned in the baghouse as is usually done. The unburned dust contains large amounts of lead sulphate and atomically fine volatilized lead sulphide, and if unburned dust is added there is little opportunity for the PbO-PbS reaction to take place.

One interesting result of double sintering lies in the effect on lead blast-furnace operation. If, as at some plants, the entire blast-furnace charge is sintered, the blast furnace merely becomes a melting device, and a remarkable increase in capacity results. The same furnace that would smelt 100 tons of unsintered charge in the old days and would smelt 250 tons of charge containing sinter has smelted up to 600 tons per day when the entire charge, including fluxes, was made up at the sintering plant and double-sintered. At the majority of lead smelters, more furnaces are standing idle than are in blast, and the furnaces actually in blast are often handling larger tonnages, owing to the sinter, than all the furnaces together could handle formerly.

Lead Sulphate in Sintering

Lead sulphate from storage-battery scrap, or lead sulphate acid sludge from acid chambers, can be sintered mixed with lead ores, or alone with carbon as fuel, and converted into a first-class material for blast-furnace feed running up to 80 per cent lead, depending on the amount of foreign matter contained in the lead sulphate sludge.

Adding carbon to sulphate alone makes an ideal charge; there being very little or no slag-forming material, aside from the ash contained in the fuel, there is no danger that the reaction will be stopped by slag coating over the metal. Sulphate treated in this way produces a rather dense sinter consisting mainly of fused lead oxide, something like burned baghouse dust but more porous, and in flat slabs. This sinter contains a fraction of 1 per cent sulphur. One peculiar feature of this particular sintering is the production of a gas high in SO_3, indicating that with carbon as a fuel $PbSO_4$ is broken up into PbO and SO_3 directly.

In the sintering of sulphate sludge, such slag as is formed is undoubtedly due to silica contained in the coal ash and possibly as impurity in the sludge itself. A very small amount of SiO_2 in finely divided form, as this is, combines readily with some of the lead oxide, and goes a long way in forming binding material for the lead oxide.

MIXING AND PREPARATION OF CHARGE

There is room for improvement in sintering as practiced today, in the mixing and preparation of the charge. Oldright points this out very clearly in his *Report of Investigations* on Smelting in the Lead Blast Furnace. Most lead-sintering plants originally used pug-mill mixers of the trough type. This was a very efficient form of mixer because it has a beating action when run at the right speeds. Lumps were broken up and the ingredients of the charge were very thoroughly intermingled. But the trough pug mill had one very serious defect—that of rapid wear of the paddles—caused by a hard lining built up by the ore inside the trough, against which the paddles must grind. This lining packed harder and harder as the paddles wore down, and not only caused undue power consumption but frequent renewal of paddles, which was expensive and lost time. Most of the charges sintered in early days consisted of table concentrates and other concentrates or ores, few of which were fine, and most of which could be made to produce sinter of a sort even if run alone, without the admixture of other ores, so that perfect mixing was not essential.

Much experimenting was done with a view to finding a mixer that would not be subject to wear, and at East Helena a mixer that is generally in use today was developed. This consists of a rotating table on which the charge is fed at the center. Over the table are placed one or more sets of rabbles made of pieces of flat steel, bolted to an arm or arms extending radially from the center of the table. These rabbles are set at an angle, so as to turn over the charge and scrape it outward from the center of the table and over the edge. Water, if needed, is sprayed on the charge as it is turned over. As long as the charges to be mixed consisted of materials not too fine, not lumpy, and most of which could be made to sinter alone, this mixer did very well—and cost practically nothing for upkeep.

Such mixers were almost universally adopted by lead-sintering plants. Where lumpy concentrates or similar materials had to be treated, disintegrators of one sort or another were installed in tandem with the mixing tables, so that the lumps were broken up and the charge given a thorough beating—which the table could not do. Where such disintegrators are used, a very thorough and satisfactory mix is obtained. The mixing table alone cannot give a really satisfactory mix with the sort of ores that compose the lead charge today.

The fact that charges are subjected to a double roast and two mixings helps a good deal, because the preroast serves to pop open or break up many of the lumps of concentrates, although at many plants a good many still may be found in the second sinter unsintered and only partially roasted.

This condition can be entirely eliminated, and an almost perfect mix be obtained, by the use of a type of pug-mill mixer in general use in zinc-sintering plants, where a perfect mix must be obtained to get results in sintering. This type of pug mill, while having all the good points of the old type, has almost none of their defects. Power consumption is very low, and paddle wear is principally confined to the last five or six paddles on the mill, where the water is added to the charge. These are very easy to replace.

The mill consists of a slowly revolving drum, inside which a paddle shaft revolves at high speed in the opposite direction. The material is fed in at one end of the drum; the paddles beat it up and throw it across the rotating drum, which carries it back into contact with the paddle shaft again. Thus the charge is repeatedly beaten up as it moves down the drum, and it comes out mixed at the other end.

Because the drum itself revolves, there is no opportunity for an abrasive lining to build up as it could in the old trough-type pug mills.

Manufacture of Acid

In the United States, no serious attempt has been made so far to utilize the SO_2 gases from lead sinter for acid manufacture. From almost any sintering machine treating lead ores, a certain portion of the gases can be selected and removed separately, which will run higher than 5 or 5.5 per cent SO_2. The sintering machine can be specially constructed and operated to make a high proportion of gas high enough in SO_2 for acid manufacture, more especially in the second roasting operation, where the charge is in a physical condition that permits the use of deep beds, which are essential to the production of a high percentage of rich SO_2 gas. However, generally this must be done at the expense of sintering capacity or low sulphur in the sintered product, as the conditions that go toward making a high proportion of gases rich in SO_2 are just the opposite of those required for producing a high output of low-sulphur sinter. Oldright has given some interesting figures on SO_2 contents of gases on both first roast and second roast machines that were not specially built or operated for the production of gas rich in SO_2. Gases as high as 15 per cent in SO_2 were found, but it is noticeable that these high-SO_2 gases were from an 11-in. bed second roast, whereas from 7-in. bed second roast the highest results obtained were a little under 7 per cent.

Standard Practice

The standard practice today seems to be to double-sinter the ore on Dwight-Lloyd machines—thus doing away with mechanical roasters. The first roast gives a quick elimination of the first few units of sulphur, which otherwise would raise the temperature too much and cause excessive fusion in the final sintering. The result is a low-sulphur sinter that makes little or no matte in the blast furnace and helps greatly to increase blast-furnace tonnages.

Blast-furnace Practice at Midvale, Utah

By Galen H. Clevenger,* Member A.I.M.E.

Equipment for treating lead ores was added in 1905 to a copper plant which the United States Smelting Refining and Mining Co. had built in 1902 at Midvale, Utah, about 12 miles to the south of Salt Lake City. By 1906 the lead section of the plant had been rounded out and consisted of a 90-ton gravity concentrator, fifteen hand-rabbled reverberatory roasting furnaces, six blast furnaces, a briquetting plant for handling flue dust and fine ores, a regulus furnace for concentrating the low-grade matte made in the blast furnaces, and a baghouse. The copper section was later abandoned and the plant has been operated for many years exclusively as a lead smelter. Some 45 years had elapsed at the time this plant was built since the first attempts to smelt lead ores in the West, and lead smelting had become a large and profitable industry but fundamentally little that was really new had been developed, which could be embodied in a plant built in this period. Principles and tools to work with had remained much the same as those borrowed earlier from European practice. Capacities had been increased and there were mechanical improvements but hand charging was still in vogue and there was little attempt to recover suspended particles carried out with the furnace gases, beyond settling in flues, which usually was only partly effective for recovery of the coarser particles. Satisfactory roasting and preparation of the fine components of the charge were still partially solved problems. The Midvale plant of 1906 may be regarded as more or less typical of the smelting plant of this period for treating complex western lead ores as distinguished from the recovery of lead from the simple lead ores to the eastward. The operation of a concentrating mill directly in conjunction with a lead smelter was, however, not common practice.

The ores treated in this plant have from the beginning come from mines owned and operated by the company or have been custom ores purchased in the territory tributary to the plant. The treatment of custom ores is an important service to the small producer who does not have sufficient tonnage to warrant a plant, and serves to increase the tonnage of the operator of large properties, thereby helping to reduce

---

Manuscript received at the office of the Institute Dec. 10, 1936.

* Consulting Metallurgist, United States Smelting, Refining and Mining Co., Boston, Mass.

costs, but unfortunately does not simplify the metallurgical problems that arise on account of the constantly changing character of the ores coming into the plant, as contrasted with a plant treating ore from a single mine or a very high percentage of ore from a single mine. The lead ores, both company and custom, treated at this plant are variable and of the complex type, as indicated by the metals recovered from them: lead, zinc, copper, gold, silver, arsenic, antimony, cadmium, bismuth and tellurium. Table 1 is given as typical of the performance of the plant late in 1906.

TABLE 1.—*Performance of Midvale Plant Late in* 1906

Roasting:

Thirteen reverberatory furnaces roasted:

	Tons
Ore	165
Matte	12
Concentrate	15
Fuel consumed (slack coal)	45 to 58

Blast Furnace:

		Per Cent		
Charge	Bed ore	35.8	Coke, per cent	12.35
	Roasted ore	18.7	Lead on charge, per cent	11.5
	Company ore	15.6		
	Iron ore (flux)	8.4	Blast pressure, oz	40
	Limestone	18.5	Charge smelted per furnace day, tons	160
	Briquettes	2.2	Bullion produced per furnace day, tons	15.1
	Scrap iron	0.8	Matte fall, per cent	5.75
		100.0		

		Per Cent		
Slag	Silica	33.9	Lead, per cent	0.9 to 1.5
	Ferrous oxide	32.0	Silver, oz	0.3 to 0.6
	Calcium oxide	20.1		
Matte	Copper, per cent			10 to 24
	Lead, per cent			12 to 24
	Silver, oz			30 to 70

Regulus Furnace:

Charge	Raw matte, tons	8.3
	Roasted matte, tons	13.0
	Ore, tons	4.0

White Metal Produced:

Content	Copper, per cent	72.7
	Lead, per cent	5.85
	Silver, oz	115.5

Robinson pot roasters were added to the plant and eventually there were 26. By the end of 1907 some of these were in operation. Table 2 shows blast-furnace performance typical of this period.

Tons of charge smelted per furnace day was only slightly greater at the end of 1907 than in 1906 but tons of bullion produced per furnace day had increased from 15.1 to 22.2. This increase is to be attributed to higher percentage of lead on the charge, 15.5 per cent against 11.5 per cent in the preceding year.

TABLE 2.—*Blast-furnace Performance in* 1907

		Per Cent		
Charge	Bed ore	42.1	Coke, per cent	13.0
	Roasted ore	10.7	Lead on charge, per cent	15.5
	Siliceous ore	6.4	Charge smelted per furnace day, tons	168.0
	Company ore	7.1	Bullion produced per furnace day, tons	22.2
	Pot roast	3.6	Matte fall, per cent	9.1
	Iron ore (flux)	0.6		
	Limestone	18.2		
	Roasted matte	7.2		
	Briquettes	3.2		
	Scrap iron	1.3		
		100.4		
Slag	Silica	35.6	Lead, per cent	0.8 to 2.5
	Ferrous oxide	30.7	Silver, oz	0.30 to 0.65
	Calcium oxide	19.8		
Matte	Copper, per cent			10 to 20
	Lead, per cent			17
	Silver			—

The next decade, or up to 1916, was occupied in making additions and changes, which eventually were to have an important effect upon the operation and performance of the plant. All of these were completed during this period except the flotation mill, which did not go into operation until 10 years later, in 1926. During the last 10 years, from 1926 and up to date (1936), improvement in blast-furnace performance shown in the accompanying tables has been due to better use of the tools at hand. The blast furnaces remained the same as those originally installed in 1906 until 1919, when the angle of bosh, which was 20° 10′, was decreased to 10° 47′, width between tuyeres increased from 45 in. to 48 in. and width at top of jackets decreased from 6 ft. 9 in. to 5 ft. 8 in. as shown, in Fig. 1. The change in bosh angle did not have an important effect upon the operation of the furnaces at this plant. A mechanical system of charging the furnaces, developed by L. D. Anderson, was installed in 1914. The principal effect of this was to save a great deal of labor.

DEVELOPMENT OF PLANT

Increased efficiency in lead smelting at this plant therefore came largely from influences external to the blast furnace and to a lesser degree from more skillful handling of the furnace, since the furnace through 30 years has remained substantially the same. Considerations of the development and evolution of the plant, which make it possible to now produce as much lead with one furnace as was formerly possible with six furnaces, some of the problems encountered and how they were solved, are briefly discussed.

Roasting and Sintering

The first addition to the original roasting equipment of hand-rabbled reverberatory furnaces was, as noted, the Robinson sintering pots. Two Wedge roasters were installed in 1912. Two more were added in 1914 and a fifth in 1925. Four Dwight-Lloyd sintering machines were installed in 1912 and two more added in 1915, making a total of six sintering machines. The hand-rabbled reverberatory roasting furnaces, sintering pots and regulus furnace were in due course abandoned.

Milling

From the beginning milling has been an important factor in the operation of this plant, permitting elimination of much gangue and zinc by a lower cost process than through the furnaces and eventually with production of much of the zinc as marketable product. The original gravity mill of 90 tons daily capacity was enlarged in 1908 to 150 tons. In 1910 the capacity was increased to 200 tons and by 1915 it had been brought up to 300 tons per day on company ore and 150 tons per day on custom ore. The gravity process when used on favorable ores, except for the slime, gave a high recovery of lead and rendered possible considerable elimination of zinc as well as gangue minerals. The zinc, however, was lost and it was not possible to decrease the iron in the lead product to the desired extent without too great a sacrifice in lead recovery. In the meantime, consideration had been given to the recovery of zinc in a salable form, but it was not until 1909 that a process was found and installed that gave promise of a satisfactory technical and economic outcome. The original electrostatic separators supplied by the Huff Company were not entirely satisfactory but after considerable investigation and modification the plant was placed on a basis of profitable operation and for the first time zinc occurring in complex western lead ores came into important commercial production. The grade of the zinc concentrate permitted shipment to zinc-retorting plants in the Midwestern gas fields. At that time none of the electrolytic plants now located in the West, which afford a more satisfactory market for zinc concentrate, were in existence. The recovery of zinc was not all that could have been desired, so that the company continued to consider as fast as they were developed various processes that promised to give a higher return. In 1910 trials were made with a chlorination process, which was intended to dissolve the zinc, and in 1916 extensive tests were made with magnetic separation, but neither of these processes proved practicable. The Huff

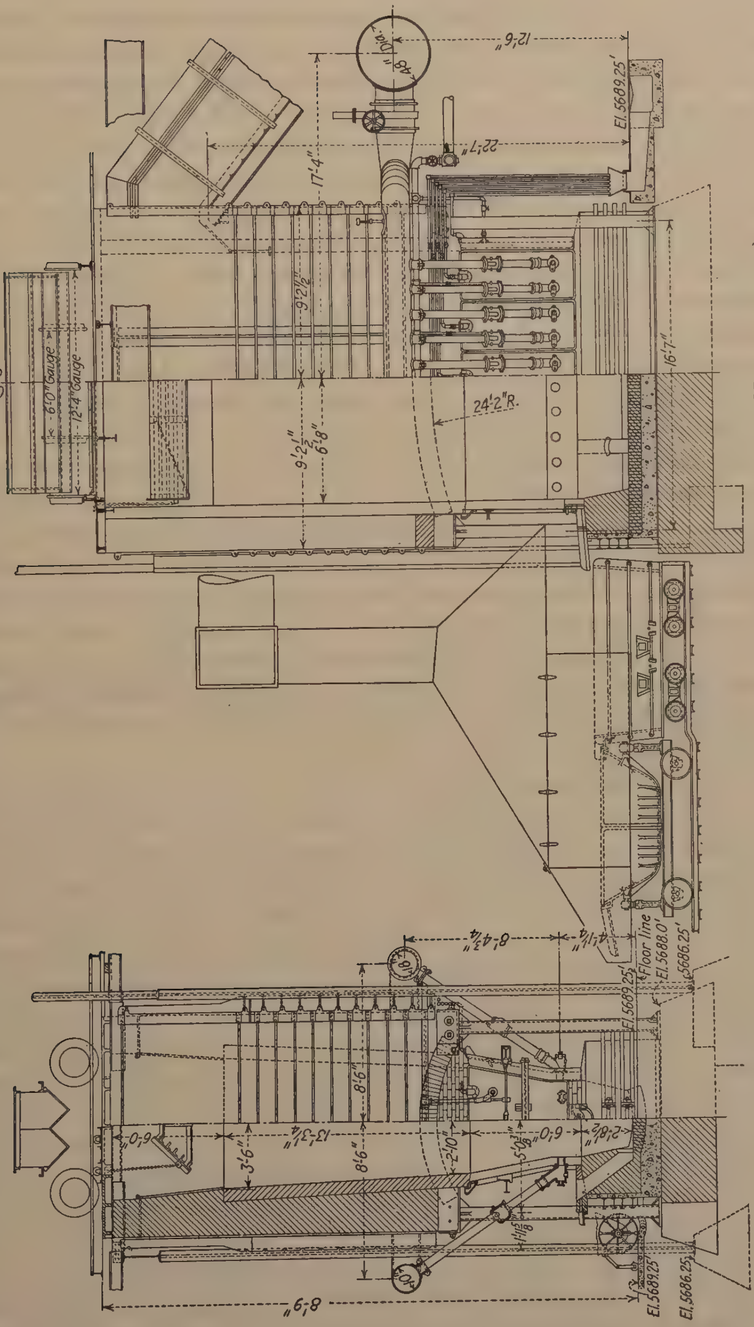


FIG. 1.—LEAD BLAST FURNACE USED AT MIDVALE AFTER 1919. (NOT TO SCALE.)

process for partial recovery of zinc was in continuous operation from 1909 until the present flotation plant went into operation in 1926. The process was used for separating a zinc concentrate from a zinc-iron middling, made by diverting a middling streak on the tables that contained only a small percentage of lead. The middling was dried and put through the Huff separators. The company ores at this time were well suited to such a process, since the lead and zinc minerals were well crystallized and there was sufficient pyrite present to form a buffer on the tables between the lead-concentrate streak and the zinc-iron middling streak. However, in order to secure good lead recovery zinc went with the lead, and also in order to secure a clean middling some zinc went into the tailing, consequently the recovery of zinc was not high but it was an important step in the direction not only of eliminating zinc but also of securing some return from the zinc in complex lead ores.

The company pioneered selective flotation of lead-zinc ores in this country at the Sunnyside mill in Colorado, but it was not until 1924 that a pilot plant was built for thoroughly investigating the application of flotation to ores coming to Midvale. The reasons for this delay were high royalties demanded by owners of flotation patents, the slow development of selective flotation to its present state of efficiency, together with the fact that there was already a process in operation that was making a partial recovery of zinc in the form of a shipping product. The large mill, which now has a capacity of 1600 tons per day, went into operation in 1926.

The Huff process was applied only to treatment of company ores having characteristics favorable to the process, whereas the present flotation mill treats all of the company ores and all custom sulphide ores. The practice at this mill has been the result of a large amount of experimental work and development. The difficulties of mill operation are greatly increased by the presence of a large tonnage of custom ore of varying characteristics. The eventual effect of the flotation mill upon operation of the blast furnace has been far beyond anything originally anticipated. It has greatly raised the grade of the lead concentrate going to the smelter. It has increased the recovery of lead, particularly from the slime portion. The zinc recovery has been greatly increased and a somewhat higher grade of zinc concentrate is produced than was possible with the Huff machines. Furthermore, it has been possible to separate pyrite, thereby keeping iron out of the blast-furnace charge when it is not needed for fluxing.

Baghouse

Filtration of a large volume of gases containing not only sulphur dioxide but also sulphur trioxide presented a serious and at the time unsolved problem, on account of the corrosive action of sulphur trioxide upon the woolen bags. This difficulty was overcome by development of a process of neutralization with zinc oxide, by C. B. Sprague. The zinc oxide was made by burning zinc ores on a Wetherill grate connected to the flue system. Later it was found that lime could be used equally well. Since it was cheaper and gave rise to less complication, standard practice has since been to feed dry hydrated lime into the flue system. All the gases from the blast furnaces, roasters, sintering machines, drossing furnaces, etc., are passed through the baghouse and into a stack 450 ft. high. Clearance of the baghouse is very high and it is possible to have at all times a clear stack with practically no visible smoke. Reverse current, hand labor, and the usual nonmechanical expedients for shaking the bags were employed until 1925, when it appeared that more baghouse capacity would be required. A simple mechanical device, which increased the filtering capacity of the bags without shortening their life, had previously been developed and satisfactorily used at the Mammoth copper plant of the company. Following experimental operation under Midvale conditions this device was installed throughout the main baghouses in 1927, and has since been in continuous and satisfactory operation. Increase in filtering capacity of the bags, secured by more efficient shaking, rendered enlargement of the baghouse unnecessary. At about the same time, the portion of the steel roaster flue system in which condensation took place required replacement. Rapid corrosion of the original steel flue made this necessary at frequent intervals. The life of this section of the flue had previously been somewhat extended by what was called the wagon-top flue. This flue had brick sides and a semicircular top of sheet steel. Cooling of the gases was secured entirely by radiation to the air and largely through the metal section of the flue, as the brick section was a fair insulator. There not only remained the corrosion of the steel in the flue, on account of condensation, but also difficulty in controlling the temperature of gases. In the summer the gases were too hot and required water sprays on the outside of the metal section of the flue to secure cooling. In the winter there was too much radiation and insulation had to be used on certain sections of the flue to conserve heat and reduce condensation. It was obvious that the only type of flue construction for this service that would have a long life would be a brick flue lined with acidproof brick, but such a flue would have a low radiation loss and therefore would not give the necessary cooling of the gases. Water sprays could be used, of course, to secure cooling in the brick flue, but there was the fear that they could not be controlled to prevent moisture in the bags. A pilot operation demonstrated that good control of the temperature could be secured by water sprays without any difficulty arising from wet bags. Accordingly, the section of the flue replaced in 1929 was of acidproof brick construction equipped with water sprays for cooling. There has now been sufficient experience with this flue system to indicate that it will have a long life and that water sprays can be adjusted to give a cooling system with the necessary flexibility.

Minor fires in the baghouse section handling blast-furnace gases may occur frequently, especially if the content of cadmium in the flue dust is allowed to rise too high. Because of the highly reducing condition in the blast furnace, these dusts contain both elemental arsenic and elemental cadmium, which explains the ease with which this type of flue dust is ignited. At times this dust will ignite when it comes into contact with the air. These fires are not serious and generally cause little damage. Far more serious are the fires that may occur, under certain conditions, in the roaster section of the baghouse. Here the sintering machines are the offenders. The action on the sintering machine is so rapid that part of the sulphur distills over as elemental sulphur, which condenses in the flue system instead of combining with oxygen to form sulphur dioxide and trioxide, which would pass out without hazard from fire. Sulphides of arsenic also distill over and appear to be as bad as the elemental sulphur. Elemental sulphur is always present in the flue dust; in fact, it does not appear possible to operate a sintering machine on a sulphide charge without formation of some elemental sulphur. Fortunately, it is possible to greatly reduce the amount of combustible elemental sulphur and arsenic sulphides formed in the sintering operation, thereby greatly reducing the hazard from sulphur fires. These fires usually start at some point in the flue system at such a distance from the sintering machine as to eliminate any possibility of the highly heated products of sintering causing ignition. The fire, once started, propagates itself along the flue and into the bags. Investigation indicates that once ignited a fire will extend through flue dust of rather low sulphur content, which would be difficult to ignite. However, when there is much elemental sulphur formed there will be localized deposits on the inside of the flue of sulphur and arsenic sulphides, containing a high percentage of these combustible substances, and which have been found can be readily ignited. These act as a primer for igniting the dust of lower combustible content, which would not have been ignited by the same cause. The exact cause of ignition is not known, but it appears that it is due either to electrical charges or spontaneous combustion. Measurements have been made which indicate that high voltages can be developed through friction between the dust particles. A record of sulphur fires follows.

The first fire causing considerable damage occurred in March, 1913, about one year after the sintering plant was built. In November of the same year there was an explosion and fire that required replacement of all the bags. Following this fire a study was made of the problem and precautions taken to avoid future fires. The next fire did not occur until January, 1925, causing the loss of but a few bags. This was followed by an explosion and fire in February of the same year. The explosion did not injure the flue system but all the bags, representing a heavy monetary loss, were destroyed by fire. Thorough investigation was made and rules laid down for operation, which it was thought would prevent future fires. Some of this information was developed after the first fires but had been overlooked through change in personnel in the intervening time.

Arsenic and Cadmium

With the baghouses in operation requiring as they did cooling of the gases to a low temperature for preservation of the bags, a closed circuit was formed for volatile, condensable elements which without the baghouse would have been bled out to considerable extent with the flue gases. This resulted in a building up of arsenic and cadmium in the flue dust even though at times there were but relatively small percentages of these elements present. A plant for producing refined white arsenic was built in 1909. Despite the very small percentage of cadmium in the charge, it would build up in the blast-furnace flue dust to 20 per cent, at which point there were frequent fires in the blast-furnace baghouse. This caused an investigation to be made to find a process that would permit of profitable production of cadmium, but it was not until 1915 that R. H. Stevens worked out the first electrolytic process for production of cadmium. This process in substantially its original form has been in continuous operation up to the present time. The ability to bleed out cadmium and arsenic without loss of the other metals solved the problem of the circulating load of these volatile elements.

By 1916 all changes and improvements having an effect upon the operation of the blast furnaces had been made with the exception of the flotation mill, which did not go into operation until 1926. In 1916 five blast furnaces were operated and at times six. Considerable oxidized ore was being received. This was screened, the plus ⅝-in. product going to the beds for direct smelting and the minus ⅝-in. being used as diluent for mixing with the calcined concentrates from the Wedge roasters and crude sulphide ore crushed to ¼ in., which made up the Dwight-Lloyd sinter charge. Single sintering then in use reduced the sulphur to 3 to 3.5 per cent. The furnace charge consisted of: bed ore 25 per cent, D. & L. sinter 42 per cent, limestone 18 per cent and iron ore 3 per cent. The analysis of a typical slag was silica 33.5 per cent, ferrous oxide plus manganese oxide 31.5 per cent, calcium oxide 20 per cent, zinc oxide approximately 6 per cent.

In 1924 the zinc oxide in the slag began to increase and reached 8.72 per cent in 1925. After the flotation mill was in operation in 1926, the slags fell back to 5.5 to 6.5 per cent of zinc oxide. With 5 to 6 per cent of zinc oxide in the slag, there had never been any difficulty in operating the furnaces, despite the fact that there was not complete oxidation of the zinc during roasting and sintering. Percentage of lead on the charge in 1916 was 12 per cent and it remained at about that point until 1926, when the beginning of operations by the flotation mill was reflected in a substantial increase, which continued upward.

The matte fall during this period was approximately 6 per cent. It was crushed to ¼ in. and a portion was passed back into the sinter charge, so as to hold the first matte at about 12 per cent copper. This precaution was thought necessary at the time in order to secure a high recovery of silver when there was only 12 per cent lead on the charge and a matte fall of but 6 to 8 per cent. The remainder of the crushed matte was roasted in the Wedge furnaces, mixed with siliceous ores and sintered. This sinter was smelted in special matte-concentrating campaigns in one of the blast furnaces to produce a matte containing about 45 per cent copper and not over 15 per cent lead, which was sold on the outside. This operation at best was not very satisfactory. In 1923 it became possible to dispose of the low-grade matte to copper smelters in the district and the concentration of matte in the blast furnace was accordingly abandoned. As time went on, the percentage of oxidized ores in the charge decreased. This and other changes are shown in Table 3. Average blast-furnace charge, blast-furnace performance and analyses of blast-furnace slag for the years 1916 to 1935, inclusive, are given in Tables 4, 5 and 6.

TABLE 3.—*Character of Blast-furnace Charge*

Year	Charge, Per Cent							
	1916	1924	1930	1931	1932	1933	1934	1935
Bed ore	25	12	10.0	7.0	2.5	2.0	6.0	5.5
D. & L. sinter	42	55	62.5	71.0	85.0	93.0	87.0	89.0
Briquettes	6	7.5	11.5	6.5				
By-products returned slag	5	7.5	7.5	7.5	5.5			
Limestone or sand	18	14	5.0	3.5	2.5	1.5	2.5	1.0
Scrap iron	1	2	3.5	4.5	4.5	3.5	4.5	4.5
Iron ore	3	2						
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Roaster baghouse dust, certain fine ores and other fine products were briquetted. Percentage of briquettes on the charge usually amounted to 6 or 7 per cent until 1930 when it increased to 11.5 per cent. The briquette press was closed down in 1931 and since that time everything formerly briquetted has been incorporated in the charge to the Dwight-Lloyd sintering machines. Dross from the bullion kettles was fed back to the blast furnaces up to 1929 when a reverberatory drossing furnace was built. The disposal of dross by the simple expedient of circulating back through the blast furnace had not caused any trouble up to this time but with increase in copper going with the lead rather than into matte there built up a hard dross on the bullion kettles, which was difficult to break up and almost impossible to skim. With the dross furnace in operation, these difficulties disappeared. There was further increase in copper and zinc in the charge due largely to an increased tonnage of ore going to the mill somewhat higher in copper and from which the zinc could not be as efficiently separated. Difficulties arising from accretions in the blast furnace due to increased zinc in the charge in 1930 rendered it necessary to eliminate sulphide zinc from the charge as far as possible through more complete oxidation during sintering. This was possible with double sintering. In 1931 matte fall was cut in two by adding crushed limestone to the second-over sinter charge. Difficulty, however, arose from breaking up of the sinter by slacking of the lime it contained. The objective in sulphur elimination was not reached until 1932 when lime sand, a natural product from the shores of Salt Lake, which had been previously substituted for the crushed limestone to overcome the difficulty from slacking of lime formed in the sinter, was added to the first sinter. Sinter produced in this way contains less than 2 per cent of sulphur. With this sinter matte fall in the blast furnace was completely eliminated

TABLE 4.—*Average Yearly Blast-furnace Charge*

Year	Bed Ore, Per Cent	Sinter, Per Cent	Foul Slag, Per Cent	By-products, Per Cent	Limestone or Lime Sand, Per Cent	Iron Ore, Per Cent	Scrap Iron, Per Cent	Miscellaneous Re-treated Material, Per Cent	Coke Used, Per Cent
1916	24.14	41.91	0.49	2.41	17.27	3.04	0.80	9.94	12.29
1917	25.53	38.57	0.06	3.95	18.96	3.79	0.08	9.06	13.02
1918	21.77	39.56	0.30	4.97	19.37	4.33		9.70	13.86
1919	19.23	41.63	0.31	5.35	18.25	4.50	0.06	10.67	13.42
1920	27.17	38.42	0.70	5.55	14.75	2.23		11.18	13.57
1921	12.06	42.93	0.33	5.49	18.50	4.85	1.67	14.17	12.80
1922	12.78	45.09	0.77	6.42	17.66	1.78	3.70	11.80	12.37
1923	13.11	47.53	0.60	6.34	19.39	3.10	1.86	8.07	13.59
1924	11.61	50.46	4.92	6.23	13.60	2.40	2.15	8.63	12.63
1925	12.34	46.98	5.72	7.20	12.70	3.99	1.33	9.74	12.35
1926	14.74	41.27	6.64	9.41	14.26	0.49	2.23	10.96	12.08
1927	16.35	44.33	2.90	7.46	16.54	0.16	2.45	9.81	12.96
1928	17.17	48.47	1.88	8.16	11.19	0.23	3.12	9.78	12.97
1929	15.76	50.08	3.45	5.98	10.26	0.17	2.97	11.33	13.32
1930	9.75	50.68	7.24	8.20	4.82	0.33	3.48	15.50	12.42
1931	6.63	52.13	13.11	8.22	3.41	0.31	4.84	11.35	12.09
1932	2.22	60.97	15.44	5.44	2.47	0.07	4.55	8.84	11.94
1933	2.17	66.05	0.38	10.98	1.51		3.55	8.60	10.35
1934	6.02	83.62	0.31		2.57		4.67	2.81	11.25
1935	5.36	85.95	0.79	1.10	1.03	0.01	4.53	1.23	10.18

and only a small speiss fall remained. At the time this change took place there was a remarkable decrease of silver in the slag, which was already low.

TABLE 5.—*Average Yearly Blast-furnace Performance*

Year	Average Number of Furnaces in Blast	Average Tons Charge Smelted per Furnace Day	Average Tons Bullion Produced per Furnace Day	New Lead on Charge, Per Cent	Slag per Ton New Lead, Tons	Matte Fall, Per Cent	Speiss Fall, Per Cent	Matte Plus Speiss Fall, Per Cent	High-grade Matte Made, Per Cent	Matte and Speiss Made in Dross Furnace, Per Cent
1916	5.36	232.5	26.1	12.16	4.91	6.51			1.22	
1917	5.92	230.6	23.5	11.21	5.70	7.18	0.24		1.03	
1918	5.35	226.6	23.0	11.16	5.61	7.84	0.48		0.78	
1919	3.98	226.9	22.4	10.50	6.03	8.78	0.31		0.86	
1920	3.98	216.1	22.6	10.84	5.66	8.62	0.66		0.62	
1921	3.92	218.5	19.3	8.98	6.63	10.93	1.03		0.82	
1922	3.84	235.3	22.9	10.35	5.99	8.68	2.40		1.53	
1923	5.40	217.1	21.3	10.62	5.76	6.54	1.51			
1924	4.68	220.0	23.6	11.59	4.87	6.44	0.86			
1925	5.22	236.4	26.4	12.14	4.59	6.51	1.34			
1926	4.92	231.0	27.6	12.56	4.37	6.34	1.53			
1927	3.93	232.2	33.6	15.28	3.44	5.25	2.45			
1928	2.15	260.9	49.3	20.07	2.50	7.26	2.13			
1929	2.05	266.4	53.6	20.73	2.42			6.03		0.40
1930	1.73	242.2	59.3	24.96	1.81			7.25		1.07
1931	1.16	277.3	81.5	29.72	1.13			5.01		1.04
1932	0.85	329.8	111.2	33.47	0.99			2.25		1.01
1933	0.60	435.9	155.2	35.15	1.07		1.55			0.49
1934	0.71	400.0	152.5	29.35	1.55		2.70			1.98
1935	0.64	472.1	153.6	33.38	1.34		2.62			2.33

Résumé

The Midvale plant has for 30 years treated complex lead ores containing zinc, a large percentage of which were and now are custom ores of variable composition.

Milling has always been an important adjunct to smelting. This has kept a part of the zinc and gangue out of the furnaces that otherwise would have gone there. Recovery of at least part of the zinc in a marketable product began in 1909 with installation of Huff electrostatic separators, which continued in operation until 1926, when there was increased recovery of zinc by the flotation process that had superseded the Huff process. For a number of years this was the one example of important and sustained commercial recovery of zinc from complex lead ores. Roasting in hand-rabbled reverberatory furnaces was early supplemented by pot roasting and these gave way in due course to multiple-hearth roasters and Dwight-Lloyd sintering machines. Hand charging of the blast furnace was displaced by a satisfactory method of mechanical charging, which saved a great deal of labor. Operation of the baghouse was rendered practicable by development of a process for neutralizing the corrosive sulphur trioxide contained in the gases. Difficulties arising through building up in the flue dust of condensable volatile impurities were overcome by building a plant for producing white arsenic and development of an electrolytic process for recovering cadmium. The use of the baghouse was eventually extended to all the gases produced by the plant. Baghouse fires and their causes are discussed.

TABLE 6.—*Average Yearly Slag Analyses*

Year	Au, Oz. per Ton	Ag, Oz. per Ton	Copper, Per Cent	Wet Lead, Per Cent	Silica, Per Cent	Alumina, Per Cent	Ferrous Oxide Plus Manganese Oxide, Per Cent	Calcium Oxide, Per Cent	Magnesium Oxide, Per Cent	Barium Oxide, Per Cent	Zinc Oxide, Per Cent	Sulphur, Per Cent
1916	0.00055	0.510	0.16	1.13	33.01	3.30	33.24	18.90	1.77	0.38	6.18	1.37
1917	0.00058	0.470	0.14	1.21	33.50	3.36	32.24	20.35	2.29	0.18	5.42	1.00
1918	0.0072	0.350	0.15	1.24	33.09	3.47	32.09	20.59	2.24	0.17	5.64	1.12
1919	0.00104	0.520	0.16	0.93	32.83	3.18	33.75	19.14	2.21	0.21	6.19	1.26
1920	0.00101	0.490	0.18	0.90	32.72	3.30	33.21	18.67	2.97	0.19	6.54	1.15
1921	0.00097	0.625	0.17	0.92	33.6	3.15	34.94	20.4	1.81	0.16	5.30	1.07
1922	0.00073	0.519	0.16	0.90	33.3	2.70	33.92	19.5	1.99	0.14	6.03	1.08
1923	0.00059	0.569	0.15	0.92	32.9	3.03	34.03	19.9	2.08	0.13	5.57	0.98
1924	0.00057	0.538	0.16	0.94	30.1	3.10	37.89	16.1	1.71	0.11	8.48	1.15
1925	0.00051	0.488	0.15	0.88	30.4	2.66	38.20	15.9	1.83	0.10	8.72	1.07
1926	0.00053	0.38	0.14	0.85	32.2	2.88	35.03	18.9	1.79	0.085	6.80	1.025
1927	0.00044	0.339	0.14	0.89	33.0	2.74	33.51	20.7	1.82	0.06	5.60	1.30
1928	0.00035	0.32	0.16	0.90	30.7	2.75	38.72	15.9	2.35	0.02	6.80	1.32
1929	0.00033	0.25	0.16	0.94	29.4	2.76	39.10	16.8	2.41	0.02	6.48	1.60
1930	0.00031	0.21	0.20	1.05	27.4	3.12	39.41	14.0	2.67	0.045	10.1	1.725
1931	0.000365	0.22	0.21	1.04	26.7	2.96	40.29	13.3	1.63	0.21	11.0	2.1
1932	0.00033	0.115	0.14	1.08	26.5	3.17	40.30	14.3	1.39	0.20	10.8	1.9
1933	0.00043	0.054	0.11	1.00	24.9	3.71	39.72	15.0	1.21	0.15	12.3	1.46
1934	0.00079	0.059	0.14	1.02	27.63	3.61	36.78	18.37	1.28	0.14	9.23	1.40
1935	0.00079	0.058	0.16	0.95	25.51	3.73	37.70	17.43	1.37	0.13	10.93	1.68

The smelting process of 1906 was a two-step operation. Low-grade matte made in the blast furnaces was roasted and smelted in a reverberatory furnace (called a regulus furnace) to give a high-grade copper matte. The reverberatory was superseded by the blast furnace for concentrating the low-grade matte. This was still a two-step operation but became a single-step operation in 1923 when it became possible to dispose of the low-grade matte without concentration, to copper plants in the district. Up to 1929 kettle dross was fed back to the blast furnace but with increasing sulphur elimination in sintering and consequent decrease in matte fall it was no longer possible to dispose of kettle dross by feeding back to the blast furnace. There was therefore return to a two-step operation, again involving the use of a reverberatory furnace (but now called a drossing furnace). Increase in zinc because more refractory ore was going to the mill caused formation of accretions in the blast furnace. This was corrected by further elimination of sulphur during sintering, causing zinc more completely oxidized to pass into the slag. Matte formation in the blast furnace ceased entirely and speiss formation was reduced. As a consequence most of the copper was forced to go with the lead, thereby further increasing the amount of kettle dross. There was no great change in the percentage of lead on the charge until the flotation mill went into operation, when there was a large increase. Previous increase in milling facilities had about kept pace with the tendency of the lead content in crude ores coming to the plant to decrease. During periods when scrap iron was high in price little was used but at the normal price it is found advantageous to use up to about 4.5 per cent.

Briefly, present practice is to mill all low-grade sulphide ores and ores containing zinc, removing as much zinc and gangue as possible and reducing sulphide iron content to the fluxing requirement. So far as practicable all components of the charge are incorporated in the sinter and sulphur is reduced by double sintering to 2 per cent or less, in order that zinc will be oxidized and slag freely. A comparatively large percentage of kettle dross is smelted in a reverberatory furnace with sulphides to give a high-grade matte and base bullion which is combined with that separated from the dross in the kettle.

Acknowledgment

The development of the milling and lead blast-furnace practice at Midvale extending as it does over a period of 30 years represents the contributions of a number of men, some of whom are no longer at the plant. Mr. Robert Wallace, General Superintendent and Mr. J. L. Meyers, Blast Furnace Superintendent, together with their coworkers, are responsible for the great increase of blast-furnace efficiency in recent years. Mr. R. A. Pallanch and his predecessor, Mr. C. A. Lemke, have made important contributions to the milling. I wish to acknowledge the cooperation of Mr. Wallace in collecting the data for this paper.

Lead Blast-furnace Practice at Trail, B. C.

By G. E. Murray,* Member A.I.M.E.

Lead blast-furnace work at Trail is unique in that this is the only plant in the world where blast-furnace smelting on a large scale for both lead and zinc recovery is carried on under one management. On this account the factors that determine economic practice differ from those of other lead smelters. In addition to this different metallurgical outlook, a great deal of structural investigation has been carried on, which has resulted in the development of a furnace which should prove of interest to all who are faced with similar problems. This description may be conveniently divided into various heads as follows: (1) General—make-up of charge, etc.; (2) structural—(*a*) hoods and charging methods, (*b*) shaft construction, (*c*) crucible construction; (3) handling slag; (4) handling bullion; (5) metallurgy.

The Charge

The Trail plant is an old one, on a congested site. As with most old plants, this limits the method of charge preparation. In general, lead metallurgists will agree that sinter when it reaches the blast furnace should contain as small an amount as possible of actual fines. There would be some difference of opinion as to the maximum size as well as of the minimum required, but to obtain the optimum condition some form of screening is indicated. This screening should take place immediately before the blast furnace if possible, and because sinter deteriorates in storage there should be as little as possible. There should also be the minimum amount of handling between the sinter machines and the furnaces.

Unfortunately, at Trail the sinter must be handled considerably before it is charged to the furnace, and no feasible scheme of screening has yet been devised. Trail practice, then, demands that the sinter be a strong one physically. Dependent upon the amount of lead in it, it has been found advantageous to incorporate granulated slag into the final sinter, the amount varying inversely as the lead content. The addition of this slag makes a harder sinter, which arrives at the blast furnace in a better condition, but it entails some lack of efficiency, because desulphurization is not so rapid nor so complete.

Manuscript received at the office of the Institute July 13, 1936.

* Chief Metallurgist, Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C.

The blast-furnace charge is made up from a number of bins provided with pan conveyors or belts, which deliver into center-dump hoppers supported on weigh beams. Each ingredient of the charge is weighed from a bin into three hoppers. The charge train, consisting of six 48-cu. ft. V-bottom cars attached to an electric locomotive, is spotted under the proper hoppers and the charge is made up as required. A typical charge consists of:

	Pounds		Pounds
Sinter	2,550	Slag shells	200 to 400
Wet slimes from zinc-plant residue or smelter flues	300	Refinery by-products	25
		Dross	50 to 75

Coke, 9 to 11 per cent

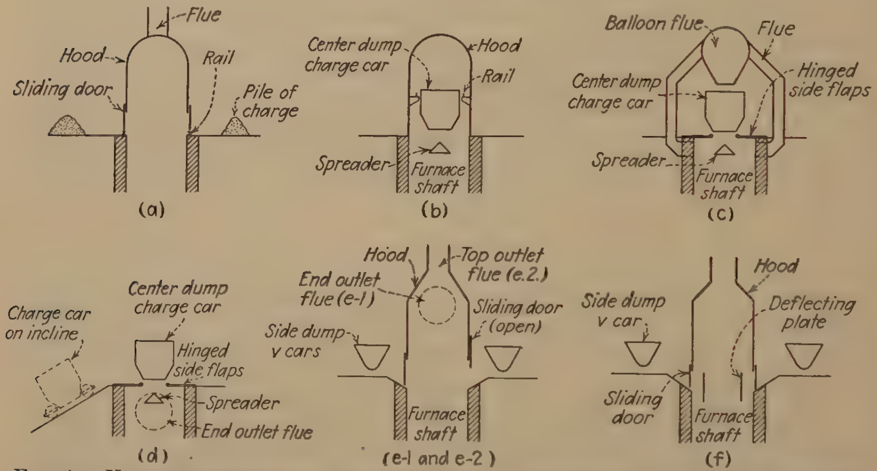


Fig. 1.—Various methods of charging and of handling gas at Trail smelter.

It has been noticed that the pan conveyors used on the sinter act as effective crushers. If possible, therefore, if a bin system is required, it would be better not to use a conveyor but to feed directly into the weighing hopper.

Hoods, Flues and Charging Methods

The problem of feeding a lead furnace has been studied for many years at many plants. At Trail many types of hoods and feeders have been used. An incomplete list of the most important of those tested includes the following, which are illustrated diagrammatically in Fig. 1:

a. Hand feeding with furnace hoods above the floor.

b. Center-dump feed cars running into furnace hood above the feed floor. Feed distributed by various types of spreaders.

c. Feed cars running over center of furnace. Gas offtake under feed floor at both sides of furnace. Spreaders used.

d. Charge car, filled by other cars, hoisted to center line of furnace, feed dumped on spreader, gas offtake at one end of furnace below feed floor.

e. V-bottom cars dumped on to inclined feed plates outside furnace hood. Hood above feed floor with (1) horizontal gas offtake at one end of hood (2) with inclined gas offtake at center of top.

f. As in *e*, above, with baffle plates inside furnace to mix and distribute the charge.

After years of experimentation, system *e*-2 is now used with a modification in the manner of filling the V-car with charge, which will be mentioned later.

The reasons for the adoption of this system of feeding and this hood (see sketch of No. 10 furnace, Fig. 2) are mainly two: (1) the ease with which the whole top of the furnace is accessible for top barring and for working while the furnace is running; (2) other things being equal, the furnace gases can be handled with less draft and consequently less leakage. For instance, with the furnace blowing badly the feed floor is clear of smoke with a draft of 0.02 in. in the main flue behind the furnaces.

The furnace hood has vertical sides, a sloping top, and a 9-ft. diameter outlet at the center of the top. The frame is of structural steel with 9-in. brick curtain walls supported by water-cooled girder beams protected by cast-iron plates, as experience has shown that in time water-cooled beams corrode in the furnace gases without protection. The sloping top of the hood is of corrugated iron, to allow for expansion.

Water-cooled doors suspended and operated by individual air-lift cylinders give access to the furnace top where necessary. Each door has flexible water connections and, together with the water-cooled portions of the hood, is connected to a Nesmith vaporizer on the main hood frame.

The offtake flue is of the gooseneck type and is practically self-cleaning, though openings are provided for lancing with air to clear any accumulated dust or accretions at the saddle.

On practical grounds, where hot gases have to be handled, particularly when a furnace happens to blow, any system that has a gas outlet below the feed floor at one end of the furnace is not a good one, and the longer the furnace, the worse it is. Furnaces with gas outlets below the floor but at the sides of the furnace are better, but are still open to objections. Unless the furnace is very high the outlets tend to fill up with charge and more draft is required to keep the feed floor clean than in the type of hood favored at Trail.

This leaves the thimble top as the main competitor for the best practical hood, at present, with the thimble extending above the feed floor and having its connection to the main flue at least above the level of a man's head. A recent study of two plants using thimble tops showed that one of the main benefits claimed for the thimble—the cutting down of leakage—failed to function. In both plants the thimble was uncovered a large part of the time, and certainly when hot tops and blowing occur there is much more smoke on the feed floor than with a hood like that shown here. Many friendly arguments have taken place centering around the question "Why the thimble?" but no arguments have yet been

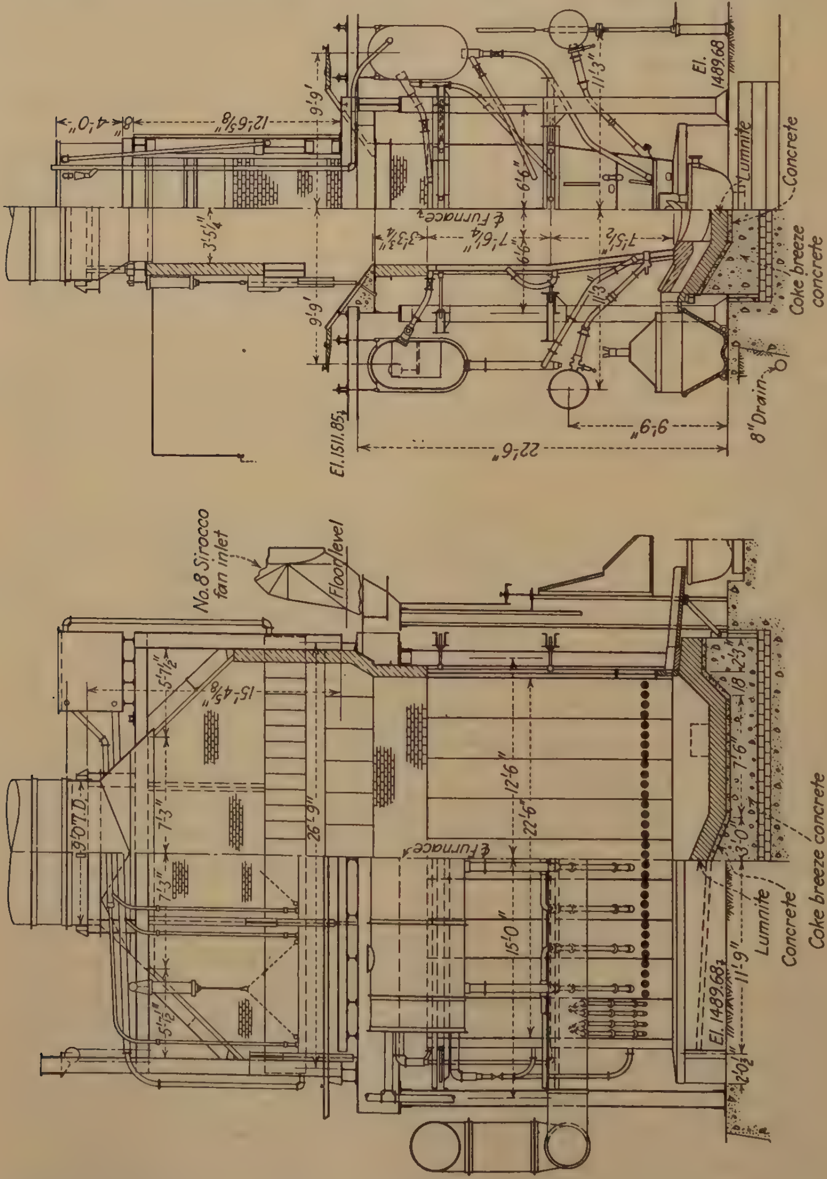


FIG. 2.—No. 10 LEAD BLAST FURNACE AT TRAIL, B. C.

advanced that would lead at Trail to a change in the design shown. It has all the advantages of the thimble as far as charge distribution is concerned (it is generally agreed that the spreader or center-charge system is not good) with the added advantage that the height of column can be varied with no increase in the amount of leakage. In barring (which, unfortunately, is necessary in all furnaces), a man standing vertically over his work can do more than one working at an angle, and access to the whole furnace is given by the large door in the rear. It is possible that given a furnace that did not hang, crust up, or blow at times, the thimble might be preferable. But no furnace has yet been developed that will always operate perfectly running with a 50 per cent lead sinter and 18 per cent zinc in the slag.

Messrs. Oldright and Miller, in cooperation with the staff at Trail, investigated various modifications of method *e*-2. The results are reported by the U. S. Bureau of Mines in *Report of Investigations No.* 3246. It was determined that one of the disadvantages of the method of charging at Trail was the tendency for the charge to segregate, owing to the difference between the specific gravity of coke and sinter. The investigations show the steps that were taken to overcome this difficulty. The most important was the splitting of the charge in each car into two parts, each with half the coke, and the placing one-half of the charge in the bottom of the car instead of all the coke (Fig. 3). In this way the heavier charge falling on the plate after the lighter coke carries it farther into the furnace and thus a good mixture is obtained. The second step taken was to use a curtain against which the charge would hit and fall vertically into the furnace. In this manner, at any height there would be the same distribution of charge. Results have proved, however, that it is much better to run with the furnace full most of the time than with a low column, and other means that will be disclosed later have given the results that it was hoped to obtain by running with a low column and without its disadvantages.

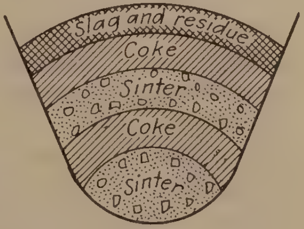


FIG. 3.—SPLIT CHARGE SYSTEM OF FILLING CARS AT TRAIL.

One feature of Trail practice not encountered in many smelters is the charging of wet residue from the zinc oxide leaching plant and the filtered discharge of the Cottrell humidifying flues directly to the lead furnaces. On account of the manner in which the V-bottom charge cars are filled, this material, containing more than 30 per cent moisture, is charged from only one side of the furnaces. In this way it does not tend to stick to the charge plates as much and gets more into the center of the furnace, where it has a better chance of becoming mixed with the charge. Naturally, it works better with good hard sinter than with a lot of fines.

In *R.I.* 3246, U. S. Bureau of Mines, some tests show that this material slowed up the furnaces. This has not been borne out over a number of years. No difference can be found with or without it, up to about 10 per cent of the total charge.

SHAFT CONSTRUCTION

For many years, and particularly during the time that Messrs. Oldright and Miller worked at Trail, much discussion took place about the reasons for the vagaries in smelting rates that will occur when a battery of furnaces is running on the same charge. It was established that the smelting rate, other things being equal, was more dependent on the length of effective tuyere zone than on the area. It was also established, as was to be expected, that a high column of charge acted as an effective dust filter. Working with charges high in zinc, however, and particularly with sinter high in lead, with a consequent low slag fall, a considerable amount of zinc is reduced, which with the characteristics of the sinter interferes with the even descent of the charge. Some of this zinc recombines with sulphur and deposits as accretions or on the descending charge. This is shown at Trail very clearly, as this secondary zinc sulphide is quite different from that of the characteristic marmatite of the Sullivan ore.

It was thus concluded that the critical zone in a lead furnace shaft was at some point above the tuyeres where the sinter passed through a pasty state. At this zone, then, much of the fume made lower down in the furnace would tend to deposit, making matters worse and tending to more irregularities. Anything that could be done to weaken the tendency to arch at this zone should give better and more regular running. Two obvious ways of breaking down this tendency to bridge were thought of. First, by increasing the width of the furnace the arch would become weaker; second, the more weight on the bridge, the less it would tend to become permanent. In other words, a wide furnace with a high column should be an advantage. To test this theory a furnace was rebuilt. Limitations due to building dimensions already in place confined the width that could be used, but the furnace was made 270 in. long and 63 in. wide at the tuyeres and, perhaps more important, 5 ft. 8 in. above the tuyeres the width was increased to 84 in. as against 69 in. in other furnaces.

When this furnace was started it ran excellently, giving a smelting rate of approximately 30 per cent more than a similar but narrower furnace. Unfortunately, another innovation had been incorporated in the furnace design at the same time. At Trail, running with dirty slags, i.e., about 3.5 per cent lead in the slag, it had been determined that the main difficulty in getting more air into the furnace was the size of opening that could be punched in the tuyere. Obviously there was no sense in having a 4-in. opening through the furnace jacket if just inside the jacket this became reduced to 1 in. More openings seemed to be the answer and as a slot that would give the greatest possible tuyere opening was considered impracticable the next best thing was done; viz., to put in as many small tuyeres as possible. There were then installed thirty-six 2½-in. tuyeres per side instead of eighteen 4-in. ones. The question then became how much of the increased speed was due to the small tuyeres and how much to the wider furnace.

To settle this point, a furnace of similar length was taken and fitted with small tuyeres, and very little increase in tonnage was obtained. To prove this point the same thing was done with two furnaces 180 in. long, and again the same result was obtained. The wider furnace gave much better speed and much smoother running. These results show that for a charge high in lead and zinc the furnaces of the past have been too narrow for the best work. What the optimum width would be is still a point to be determined. The fusibility of the charge would have some effect on the proper dimensions, no doubt. The less fusible the charge, the less would be the tendency to bridge, one would expect. Both at Trail, where at one time a flux containing CaF_2 was used, and at other places, notably Mt. Isa, where fusible sinters containing carbonates were made, the tendency to bridge and hang was accentuated. Other furnaces as narrow as 36 in. wide seem to work excellently on low lead charges, but tend to have trouble with increasing lead in the sinter. Knowing this, there seems to be no reason for constructing lead furnaces for fusible sinters with a bosh, or a slope that tends to help the formation of bridges. Vertical sides should be preferable, and apart from structural difficulties many arguments could be advanced for building them wider at the base than at the top. For one thing, this would increase the reservoir of coke and concentrated reducing gases, which Oldright and Miller have shown to be present at the tuyere zone in the middle portion of a lead furnace running well.

Effect of Small Tuyeres

Furnaces that run with tuyeres always bright and open may not need the smaller tuyere to get more air into the furnace, but the results noted below would indicate that there is a better distribution of air with the smaller tuyere on a furnace running with a charge such as that at Trail. In order to prove this, experiments were run going back to the old methods of charging on the narrower furnaces with the furnace run down 6 ft. and all the coke placed in the bottom of the charge cars. This had given results as shown by Oldright and Miller as in Table 1. The method is described in detail in *R.I.* 3244. These tests show that the introduction of the small tuyere resulted in a much better distribution and utilization of the air entering the furnace independently of the method of charging.

The results of these major changes in furnace construction, it is believed, have shown that there is still something to be gained in experimenting on the fundamentals of blast-furnace work. It is hoped that some one, some time, in constructing a new furnace, will endeavor to settle the optimum dimensions for other conditions.

TABLE 1.—*Effect of Small Tuyeres on Top Gases*

Furnace	Depth of Charge below Floor, Ft.	Size of Tuyeres, In.	Description of Charge	Furnace Dimensions, In.	Average Analysis of Top Gases		
					CO_2	O_2	CO
No. 8	6	4	Coke in bottom of car	180 × 48	16.0	5.0	5.0
No. 9	6	4	Coke in bottom of car	180 × 48	13.3	8.1	4.1
No. 12	6	2½	Coke in bottom of car	270 × 48	18.5	0.8	8.2
No. 12	6	2½	Split charge coke on top	270 × 48	16.8	0.56	12.1

At Trail, above the first tier of steel jackets, there have been used: concrete shafts lined with fire brick, all-brick shafts, and all-water-jacketed shafts. Though there used to be a prejudice against the last, owing to excessive crust formation, it is now felt that this was due to the shape of the jackets in the lower tier. The best form of construction is now considered to be the water-jacketed shaft in conjunction with a Nesmith vaporizing system, the circulation in the two tiers of jackets being joined together, the water feeding to the lower jacket and the connection to the vaporizer being made from the top of the top jacket. It is known that the ordinary lead furnace with brick shaft operated with good reduction does not give the trouble that is experienced at Trail where, owing to the method of operation, the combustion zone tends to creep up the shaft. For large furnaces, however, there are many structural advantages in using water jackets. There are also operating advantages with no detrimental effects that can be determined. Using the vaporizer system even where water is scarce, the extra jacket area for the top tier requires very little, if any, additional water and has much to recommend it; all the jackets are approximately at the same temperature and the furnaceman is left to give his undivided attention to the operation of the furnace as a smelting device.

Nowhere now is there the crucible or slag trouble on a lead furnace that used to be a commonplace some years ago but there are still times when it is convenient to have a larger tap-hole either to facilitate starting up after a shutdown or to help out a temporarily bad slag. The tapping jacket developed at Trail, with a removable cast-iron plug, has been a great convenience. It is quickly and easily removed and replaced. It facilitates barring of crucible crust from the front, as it allows a bar to take an angle more nearly vertical (Fig. 4).

CRUCIBLE CONSTRUCTION

Experience had shown that it was necessary to have a reservoir for bullion only in the crucible at the front of the furnace. For some years the practice had been to fill the back part of the crucible shell and to leave a reservoir as shown in Fig. 2. The crucible has been constructed as described below in detail. For practical purposes, it is now a block of concrete, and so the usual crucible shell with its heavy reinforcing and staying is unnecessary. The shell now is practically a form.

The crucible is elliptical in shape. The shell is of ¾-in. flange quality steel plate with riveted butt straps and ¾ by 6-in. reinforcing mild steel bar at the top. It is set in a ¼-in. welded steel pan over a 9-in. brick fill

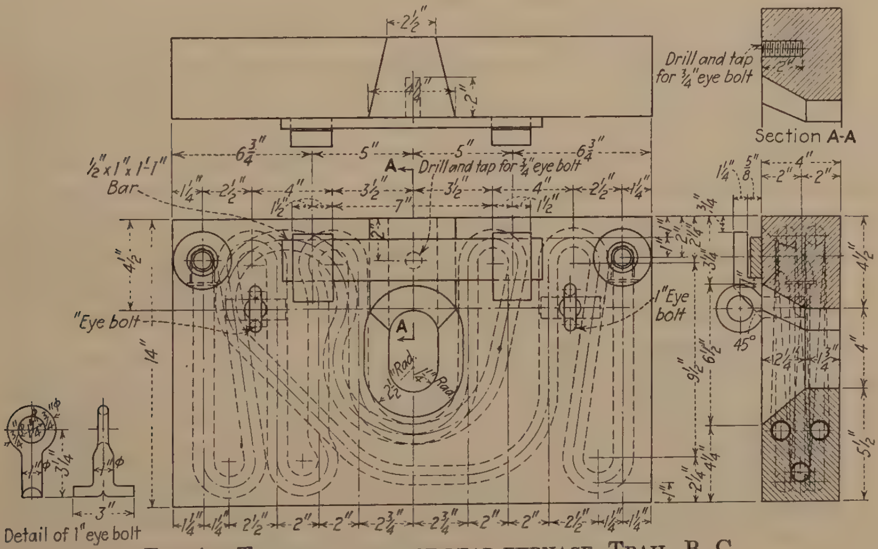


FIG. 4.—TAPPING JACKET OF LEAD FURNACE, TRAIL, B. C.

in the foundation. Around the inner periphery, vertical 60-lb. steel rails are spaced to take the thrust from the jackets. Two rails extending the full depth of the shell are used for each jacket.

The main body of the crucible is filled with coke-breeze concrete made of 1 part cement, 2 of sand and 3 of coke screened through a 1-in. ring. Above this there are 3 in. of Sil-O-Cel C_3 concrete, then the refractory lining is formed to the required shape. This is made of 12 in. of lumnite concrete made of 1 part of lumnite cement to 4 parts of crushed brick.

HANDLING SLAG

Before the introduction of slag fuming at Trail, the slag was granulated and stored awaiting the development of a process for the recovery of its zinc and lead. When slag treatment started it flowed into 9-ton transfer pots, which, when filled, stood around till the blow on the previous batch was finished. This resulted in a large amount of slag shell being formed, which had to be resmelted or treated cold in the slag-fuming furnace. As treating coarse, cold slag cuts the capacity of this furnace greatly, it was decided, after many failures to reduce the amount of shell made, to tap into reverberatory furnaces fired with powdered coal, where the slag could be held molten until required. These furnaces are described in the paper by R. R. McNaughton (p. 721, this volume).

One interesting feature of the operation of these furnaces from the point of view of the lead metallurgist is the fact that even in a coal-fired chamber there is a settling out of a material that will gradually fill up the furnace as a mush. An examination of this showed it to be largely composed of spinels. Calculations show that there is a concentration of spinels in this mush of about four times that in the slag.

At times, particularly when the silica in the slag is allowed to get too low, the holding furnaces tend to fill up rapidly. The procedure adopted to overcome this is to tap the furnace dry and to burn an excess of coal to give a reducing atmosphere, and to blow sand on to the surface of the mush. This makes it fluid enough to take out of the furnace. Ordinarily this procedure is followed every time a charge is made up for the slag-fuming furnace, or about every 2½ hours.

Handling Bullion

Bullion that flows continually from the lead wells is first caught in a receiver and then laundered to the furnace craneway to cast-steel pots containing about five tons each. The pot is then transferred to the drossing plant.

At the drossing plant the bullion is poured through the roof of either of two drossing furnaces fired with powdered coal. These furnaces have a capacity of 100 tons each and each uses 2.2 tons of powdered coal per day. When a furnace is full the dross bath is at a temperature of 1300° F. and the bullion at 1000° F. The dross is skimmed from doors along the side into pots that have holes in the bottom, which allow most of any bullion skimmed to flow through the pot and collect into a bed under it. The bullion that collects here when solid is remelted in the pots. In this manner a good dry dross is obtained. This dross is re-treated in the blast furnaces until it is sufficiently high in copper to warrant treatment in the dross re-treatment furnace. Ordinarily it is returned to the blast furnaces for two days and stored on the third day.

The bullion from the drossing furnaces flows into a series of three pots holding 60 tons each and finally is pumped to the casting pot of 100 tons capacity, where the final cooling takes place, if necessary by the addition of cold lead, to a temperature of 650° to 700° F.

The device used at present to insure uniformity of anode weights consists of a 12-in. section of 10-in. steel pipe open at the top and coned down to receive an open plug cock. Bullion is pumped into this device to a level fixed by a gauge point and the operator swings a lever turning the plug cock and emptying the contents of the measure into the mold through a perforated baffle plate, thus reducing the tendency to form fringes along the sides of the mold. The weight variations between anodes can be held within 2 per cent when casting 400-lb. anodes.

The casting wheel is 18 ft. in diameter, motor-driven by worm gear and friction clutch to make one revolution in just under 5 min. There are 16 cast-steel, two-piece molds hinged to break at the junction between the lugs and the body of the anode. As the wheel revolves the anodes pass under a water spray and are then flattened by means of an automatic air hammer. At this point a guide rail engages with the lug section of the mold and lowers it sufficiently to allow the anode to be lifted out and loaded into cars for transfer to the refinery. At present, 200 anodes per hour can be cast.

Naturally, in cooling the pots described above, more dross is made. This is skimmed off with perforated iron shovels, loaded into pots and charged back into one of the furnaces, for sweating. In this manner no particular care need be taken about letting the bullion picked up with the dross drain off. The only dross that has to be re-treated is that dry dross skimmed from the drossing furnaces.

It is believed that the reverberatory method of drossing has many advantages. It is theoretically the right way, for in ordinary drossing from iron kettles, the lead is hot and the dross is colder. This is the reverse of what it should be. The dross that has risen to the top should be hotter than the main bulk of lead, in order to sweat as much lead from this dross as possible. Using the furnace method, the dross going to the dross re-treatment furnace ultimately is hotter and hence easier to treat, it contains less metallic lead to be subjected to the high oxidizing temperatures found in the re-treatment furnace and the heat required for the drossing operation is applied in a more efficient manner.

The furnace used for re-treating the dross skimmed from the drossing furnaces as related above is operated only intermittently, usually about every 6 months. Dross is stored and when it is decided to start a re-treatment campaign it is fed back to the blast furnaces at a rate sufficient to run the re-treating furnace to capacity. This is approximately 50 tons of hot dross per day. If cold dross is used the rate is only 30 tons per day.

The furnace used for this operation is much smaller than that found at most lead smelters, the hearth area being only 7 by 13 ft. It is fired with powdered coal and a locally designed turbulent burner is used. From 6 to 7 tons of powdered coal is burned per day and the matte or speiss produced contains about 22 per cent Pb and 56 per cent Cu.

The slag made in this furnace contains most of the tin in the lead circuit and when it was being re-treated the refinery ultimately got into trouble from the cycling load. At present this slag is being stored for future treatment. It contains on the average the metals noted below. The bullion analysis from this furnace is also given:

	Ag	Cu	Pb	Zn	S	SiO_2	Fe	CaO	Sb	Sn	As	Bi
Slag.........	0.6	3.7	37.6	4.3	0.3	11.1	10.2	2.0	4.0	2.3	2.1	0.004
Bullion......	32.7	1.7							0.58	0.25	0.52	0.039

METALLURGY

As mentioned, Trail metallurgy differs from that of other lead smelters. In reality it is a zinc as well as a lead smelter.

On account of the slag-fuming operation, the most economical charge for both lead and zinc recovery must be used, not that for lead alone. This means that the slag made must carry as much zinc as possible. The products of the Sullivan mine, which constitute the main portion of the charge, contain very little silica or lime. The lead concentrates and zinc-plant residue, which make up from 75 to 80 per cent of the charge, have the following analyses at present:

	Pb	Zn	S	SiO_2	Fe	CaO
Concentrates..............	70.5	3.9	17.4	0.83	6.3	0.8
Zinc residue..............	10.1	21.4	4.7	3.3	32.0	0.5

It follows that the slag aimed at should contain as little silica and lime as possible. Experience has shown that it is not safe to run with a slag containing less than 18 per cent SiO_2. It has also been determined empirically that from 7 to 8 per cent lime is satisfactory. This leaves zinc and iron as the remaining important slag-forming ingredients, and their ratio is determined by the analysis of the Sullivan products. For many years the slag made contained from 17.5 to 18 per cent zinc and about 30 per cent Fe. At this time the zinc to iron ratio in the lead concentrates was not more than 1:1 to 1:1.3, and frequently barren iron in the form of sulphide tailings had to be used as a flux. A change in milling practice, however, has successfully dropped the zinc, so that at times the zinc to iron ratio becomes 1 to 2. Under these conditions, of course, the zinc tenor of the slag is lowered. This increases the cost of the slag dezincing, as within limits the slag furnace burns the same amount of fuel per minute regardless of the zinc content of the slags. The surplus of iron given by the above figures would be welcomed at many plants where more margin-bearing siliceous ores might be smelted. This, however, cannot be done at Trail, as it would only serve to dilute the zinc even more. With the increased price of gold there has also been an increase in the receipts of irony concentrates, which has also tended to lower the zinc in the slag.

There is not much difficulty in controlling the lime. The iron and zinc happen, as it were, but the silica is not easy to control. The supply consists of many shipments varying in silica content from 35 to 90 per cent. With a small slag fall this makes work difficult, and with the trouble that follows when silica becomes too low the tendency of the furnace operator is to keep more silica on than absolutely necessary for good furnace conditions. The aim is to keep the slag around 19 per cent SiO_2. If it falls below 18 per cent, siliceous ores crushed to ¾ in. are added directly to the furnaces. When the analysis is below 19 per cent SiO_2, there is a greater tendency for metallic lead to occur in the slag. One of the surprising things about the Trail operations is the amount of metallic lead in the slag. Work done by Oldright and Miller (U. S. Bureau of Mines, *R.I.* 3264) shows that at times from two-thirds to three-fourths of the total lead in the slag is in the form of metallic lead. In smelter slags studied from other plants, more lead is present as sulphide.

At this point it might be well to clarify the situation in regard to the amount of lead in Trail slags. It is wrong to assume, as has been done, that the Trail practice likes to have so-called "dirty" slags. It would be worth something to be able to obtain the advantages of poor reduction with the Trail charge and at the same time run with slags containing around 1 per cent or less in lead. Before the introduction of the slag treatment, Trail practice carried the lead in the slag from 1.8 to 2.0 Pb with 17 to 18 per cent zinc. This is very similar to the practice developed at Port Pirie, South Australia. It was found that more intensive reduction tended to give irregular running and general furnace difficulties. With the slag treatment, the lead in the blast-furnace slag is about 3.5 per cent. This means that there is a circulating load of about 10 tons of material per day, which has to be resmelted. As the final lead loss in the slag from the fuming plant is negligible, it is much cheaper to handle this circulating load than to obtain cleaner slags in the blast furnaces. The furnaces run faster and with less trouble so that until a means is found to obtain these advantages and cleaner slags at practically no additional cost, the practice of running a high lead in the slag is likely to continue, although at first glance it seems uneconomical.

The analysis of the current Trail slag is, on the average, as under: Ag, 0.10 oz. per ton; Cu, 0.15 per cent; Pb, 3.5; S, 1.5; Zn, 16.5; SiO_2, 19.0; Fe, 30.5; CaO, 7.5; Al_2O_3, 5.0; MgO, 1.5; Mn, 0.6.

It has been noted, in the work at Port Pirie reported by O. H. Woodward in the Bulletin of the Institute of Mining and Metallurgy (June, 1931), that a longer tapping period reduced the lead content of the slags there. Unfortunately, repeated attempts to obtain similar results at Trail have failed although the tuyeres on the furnaces have been raised.

The coke used is all of beehive-oven manufacture. Several grades of coke have been used of varying porosities and ash contents, from 10 to 20 per unit. On the whole, very little if any difference has been noticed in lengthy tests. There have been times when the average size of the coke has been fairly large. Then it is an advantage to screen through a 6-in. screen and crush the oversize in a special type of coke crusher developed at Kellogg, Idaho. At times, too, a ¾-in. screen has been used to eliminate some of the fines, but no definite effects on blast-furnace operation or coke consumption have been noted.

Table 2.—*Analyses of Cokes Used at Trail*

Coke	Fixed Carbon, Per Cent	Volatile Matter, Per Cent	Ash, Per Cent
A	79.1	0.7	18.6
B	88.0	0.5	9.5
C	82.3	0.5	15.6

No regular analysis of the finished sinter is made, because of the difficulty of sampling. As the Trail charge is made up largely of material from one source, and as the difficulties of bedding large quantities of wet concentrates in the winter time are many, no bedding system for the sintering charge is used. As has been explained, the main control for slag analysis is the silica content, so that the charge calculations used at most smelters are little used. A daily composite sample of the crushed sinter is taken between the first and second sintering machines. The most important element in this analysis is the sulphur content, which is kept around 6 per cent. Additions to the second sintering machines other than just sinter are granulated blast-furnace slag and some wet flue dust from the Cottrell humidifying flues. The charge to the first machines contains from 49 to 53 per cent lead, 14 per cent S (before the return of crushed sinter, which is added in varying amounts), 5 to 6 per cent SiO_2, 10 to 11 per cent Fe, 3 per cent CaO, 6 to 7 per cent Zn. The bullion runs within the following limits: Au, 0.2 to 2.0 oz. per ton; Ag, 40 to 50 oz. per ton; Cu, 0.035 per cent; Pb, 98.85; Sb, 0.60; As, 0.35; Bi, 0.02 to 0.06; Sn, 0.02 to 0.05. Cottrell treater dust analyses: Au, tr.; Ag, 0.7 oz. per ton; Pb, 50.0 per cent; Zn, 13.8; S, 10.5; Fe, 0.1; Cd, 2 to 4; F, 0.3.

For the recovery of cadmium a certain proportion of the Cottrell dust is sent to the zinc plant each day. The lead is returned to the smelter with the zinc-plant residue. The Cottrell dust that is not treated for cadmium is returned dry to the Dwight-Lloyd machines, where it is most important in the sintering operation.

After experience with the operation of a slag-treatment plant, there are undoubted economies to be obtained in conjunction with the operation of a lead smelter. To obtain the maximum benefit from these economies, however, both plants should be under the same metallurgical control, so that all the factors governing the whole problem of the most economical recovery of both metals can be given the proper consideration.

Blast-furnace Practice at the Bunker Hill Smelter

By P. C. Feddersen* and H. E. Lee†

Blast-furnace operation at the Bunker Hill smelter deviates somewhat from common practice. Under existing conditions it is economical to operate the furnaces at "forced" capacity. The furnace feed consists chiefly of sinter and averages close to 50 per cent lead. Experience in smelting such material favors a low charge column attended by smaller proportions of coke and a low blast pressure. Under such conditions the gain in furnace tonnage greatly overbalances the somewhat higher slag losses and increased percentage of material fumed.

Furnace Charge

The ingredients for the blast-furnace feed are stored in a group of 24 charge bins (3600 cu. ft. capacity). Each bin has two discharge chutes. Beneath each chute is a steel weighing hopper, suspended from a Fairbanks scale. The several hoppers are kept filled with the exact amount of material required to complete a furnace charge. The weighed material is discharged into a standard-gauge, bottom-dump charge car containing two compartments, each of which holds a complete charge (approximately 1½ tons). It is hauled to the blast furnace by a 4-ton electric trolley locomotive. The proportionate parts of the various constituents of a representative blast-furnace charge are shown in Table 1.

Table 1.—*Representative Blast-furnace Charge at Bunker Hill Smelter*

Material	Pounds
Sinter	2500
Limerock	0– 50
Coke	250–300
Scrap iron	0– 25
Settler skulls	75
Undried zinc-plant residue	0–200
Siliceous ore	25
Baghouse dust	0– 50
By-product slag	100

A variable stock tonnage of zinc-plant residue and return by-products results in fluctuations in the percentages of these materials in the blast-furnace feed. Accompanying such variations are corresponding increases or decreases in the amounts of coke, limerock and scrap iron necessary to obtain good furnace operation and adequate reduction.

Manuscript received at the office of the Institute July 28, 1936.

* Assistant Superintendent, Bunker Hill Smelter, Kellogg, Idaho.

† Research Engineer, Bunker Hill Smelter.

Table 2 presents representative assays of the constituents comprising the blast-furnace feed. The sinter assay given is that of the final roast. During the roasting operation about 10 per cent of the lead content is reduced and recovered from the wind boxes. The wind-box lead is subsequently added to the final roast discharged from the pallets. This addition will increase the lead content of the sinter to the blast-furnace bins to about 50 per cent, attended by proportionate decreases, with the exception of silver and gold, in the percentages of other materials present. Silver and gold are concentrated in the wind-box lead and will thus show corresponding increased values over the assay presented.

Table 2.—*Representative Analyses of Constituents Comprising the Blast-furnace Feed at Bunker Hill Smelter*

	Material					
	Sinter	Settler Skulls	Return By-product Slag	Zinc-plant Residue[a]	Bag-house Dust	Siliceous Ore
Au, oz. per ton	0.02			0.02		
Ag, oz. per ton	25.0	2.8	75.0	9.0	3.8	25.0
Cu, per cent	0.41	0.6	2.2	0.2	0.07	0.2
Pb, per cent	45.0	5.0	31.0	10.5	60.8	15.0
Fe, per cent	13.5	27.1	17.0	22.5	0.2	2.0
Mn, per cent	0.85					
Insoluble, per cent	9.0	24.8	14.0	12.0	2.0	75.0
Al_2O_3, per cent	1.39					
CaO, per cent	7.59	10.4	1.6			
MgO, per cent	0.94					
S, per cent	1.7	2.7	1.2	7.8	7.2	1.0
ZnO, per cent	6.5		3.0			Tr.
Zn, per cent				12.0	7.0	
Sb, per cent	0.26		12.0	0.10	1.2	0.2
As, per cent	0.22		1.7	0.45	0.24	

[a] Undried zinc-plant residue contains approximately 40 per cent moisture.

As indicated by the tables, the feed to the Bunker Hill blast furnaces is characterized by a high lead content and predominant proportions of sinter. The furnace operation is thus mainly influenced by the physical and chemical nature of the sinter[1] supplied. Consideration of the effects of variations in the chemical and physical properties of sinter upon furnace operation, and other such details, is beyond the scope of this paper. Such information, with regard to this smelter, has been rather completely presented in a group of publications by G. L. Oldright and Virgil Miller[2].

---

[1] The sinter is discharged from the Dwight-Lloyd machines into standard-gauge railroad cars and transferred to the blast-furnace charge bins. No fines are removed, but a screening arrangement is being contemplated, as this step will unquestionably improve blast-furnace operation.

To maintain uniform furnace conditions, practice at the Bunker Hill smelter is to feed small charges at frequent invervals. Coke is first added to the charge car, followed by other ingredients such as limerock, return slag, zinc-plant residue, etc., and finally the sinter charge. The charge car is then hauled to the feed floor over the top of the blast furnaces. The charge is dumped, over a single railroad rail which acts as a spreader, vertically through an opening 2½ ft. wide.

The charging interval is a variable depending upon the smelting rate of the furnace. Under normal operating conditions a furnace will require a charge about every 10 to 12 minutes. Under a given set of conditions the desired charging rate is controlled by measuring the height of the column with a pole from the feed floor. Indications are also obtained from a recording pyrometer installed with its hot junction in the flue outlet.

THE BLAST FURNACES AND THEIR OPERATION

There are three blast furnaces[3] at the Bunker Hill smelter, one or two of which operate steadily. The furnaces are 48 by 180 in. at the tuyeres, with a height of 22 ft. from the crucible to the feed floor, the crucible being 45 by 180 in. The furnaces have two tiers of steel water jackets, five jackets on each side with two 4-in. tuyeres per jacket. The blast is supplied by a Connersville blower[4] having 100 cu. ft. displacement per revolution, and is driven at a speed of 145 r.p.m. The furnaces use from 5000 to 7500 cu. ft. of air per minute at an average pressure of 24 oz. The fume is conveyed through a steel flue (beneath the feed floor) from the ends of these furnaces into a large settling flue, and then to the baghouse. With a blast pressure of 24 oz., practically no fume escapes at the feed floor.

As stated at the outset, the Bunker Hill blast furnaces are operated with a low smelting column. The height maintained ranges between 8 and 10 ft. Experience has proved that, under existing conditions, the furnaces will smelt much larger tonnages than with a high column. Therefore, even though reduction is perhaps not quite as good as in a furnace operated with a higher charge column, and more fume is produced, the use of a low column is the more economical. Perhaps if the furnaces were considerably deeper, so that the charge could be carried at a higher level without danger of chocking the flue outlet, and a correspondingly higher blast pressure could be maintained, the present picture might be changed.

---

[2] G. L. Oldright and V. Miller: Smelting in the Lead Blast Furnace—Handling Rich Charges. U.S. Bur. Mines *R.I.* 3088 (1931), *R.I.* 3094 (1931), *R.I.* 3095 (1931), *R.I.* 3096 (1931), *R.I.* 3183 (1932).

[3] A furnace measuring 66 by 252 in. at the tuyeres is being constructed, similar in design to the two large furnaces of the Consolidated Mining & Smelting Co. at Trail, B.C., which have been in successful operation for several years.

[4] Two Ingersoll-Rand turboblowers are held as auxiliary units. Each has a capacity of 12,000 cu. feet.

In keeping with this method of operation, the proportion of coke utilized is that sufficient to provide economical reduction, with respect to the furnace smelting rate, and a fluid charge. Experience has indicated that optimum conditions are obtained with coke equal to about 10 per cent of the total charge weight.

After operation for about 10 days the furnace is run down and accretions are removed. The furnace column is smelted to a height of about 5 ft. above the tuyeres, then a charge of coke is dropped in and the tuyeres and lead well are plugged with clay. One top jacket is removed from both the front and back ends of the furnace and the accretions are drilled, barred, and sledged through to the top of the bottom jacket. The material thus removed is transferred to the crushing plant and thence to the roaster charge. The removal of accretions requires 2 to 3 hours.

The slag is tapped through two settlers. The first, 6 ft. in diameter and made of cast steel 2¼ in. thick, overflows into a smaller pot, 5½ ft. in diameter and 1 in. thick. The second settler overflows into a Treadwell pot of 130 cu. ft. capacity, and is hauled to the slag dump by a 10-ton standard-gage electric trolley locomotive.

An average assay of monthly composite samples of slag going to the dump during the past year is given as follows: Ag, 0.15 oz. per ton; Cu, 0.12 per cent; Pb, 1.2; FeO, 36.4; MnO, 1.6; SiO_2, 21.99; Al_2O_3, 3.8; CaO, 15.2; MgO, 1.63; S, 1.9; ZnO, 16.5.

The lime content of the slag is relatively high. The bulk of this lime enters the furnace as a component of the sinter charge (Table 2). At this plant, the improved results obtained by its presence during the sintering operation, coupled with its beneficial properties in subsequent blast-furnace reduction, have favored the use of a high-lime charge.

As might be expected from the foregoing analyses of the constituents of the furnace charge, the tonnages of matte and speiss formed in the Bunker Hill blast furnaces are relatively small. The lead, at furnace temperatures, is capable of dissolving practically all the matte and speiss formed. They are removed with the lead flowing from the furnace, segregating upon cooling as dross scum.

The lead runs through a lead well in the side of the furnace. A good-sized stream flows rather continuously into a 4-ton brick-lined cast-steel pot, which rides on a four-wheeled carriage. When filled, the carriage is pulled from the furnace by a traveling crane, then the pot is lifted and transferred to a drossing kettle. Here the lead is dumped and the pot returned for another charge.

Lead Blast-furnace Practice in Missouri

By C. M. Warner,* Member A.I.M.E.

In both the Flat River district of southeast Missouri and the Joplin district of southwest Missouri the lead concentrates are of very high grade, free of arsenic, antimony and bismuth, and contain no gold and very little silver. The general practice in both districts is to smelt the concentrates containing 70 to 85 per cent lead on Scotch hearths, to recover 70 to 85 per cent of the lead, and then smelt in a blast furnace the slag formed in the Scotch hearths to bring the total recovery of lead from lead concentrates to over 97.5 per cent.

At the lead smelter of the St. Joseph Lead Co. at Herculaneum, Mo., no Scotch hearths are used. In the other smelters in the district the blast furnace plays a minor role to the Scotch hearth.

The concentrates produced from the Flat River district are either table concentrates or flotation concentrates containing:

	Pb, Per Cent	S, Per Cent	Zn, Per Cent
Table concentrates	80.0	14.2	0.6
Flotation concentrates	72.1	14.3	2.3

Both types of concentrates are received at Herculaneum in box cars after being sampled. Great care is taken in weighing and sampling of cars of concentrates and in the determination of moisture and lead contents.

The concentrates are unloaded into bins by an adaptation of scoop grain unloader. Four men unload and sweep a 40 to 45-ton box car of concentrates in 30 minutes.

The same grade of concentrates is received each day and no metal-bearing fluxes are available. The problem is to get as high a recovery as possible as cheaply as possible from the high-grade lead concentrates produced by the company's concentrating mills.

Sintering

The bulk of the sulphur is removed from the concentrates and the fine concentrate particles are agglomerated by double roasting on typical Dwight and Lloyd sintering machines.

Manuscript received at the office of the Institute Aug. 6, 1936.

* Superintendent, Herculaneum Division, St. Joseph Lead Co., Herculaneum, Mo.

All the fine materials around the plant are put into the sintering mixture. Lead concentrates and burnt baghouse fume constitute the lead-bearing part of the charge to the sintering machines, to which are added granulated slag and small amounts of pyrites cinder, crushed matte, silica sand, flue dust and tailings, or fine particles screened from the finished sinter through a grizzly.

The mixture to the sintering machines is apportioned by feeders on to a collecting belt, and is not weighed. The analysis of the final sinter governs the adjustments of the feeders, and the finished sinter can be held to a high degree of uniformity both as to chemical analysis and structural strength.

In earlier practice barren fluxes were used entirely to dilute the lead concentrates to a mixture that would make a good sinter, and only one sintering operation was considered necessary. The use of granulated slag cut the cost of fluxes and the granulated slag carried its own lead loss. It is cheaper to spend money on the sintering process and secure a better product for smelting in the blast furnace. In double sintering the lead content of the finished sinter is raised and a lower sulphur content and a stronger sinter are obtained. The crushing of the first sinter exposes fresh sulphide particles that have melted and not oxidized, rendering a more complete desulphurization possible.

The use of granulated slag instead of barren flux, the increased tonnage over the sintering machines, the mechanical improvements in handling the sintering mixtures, have resulted in the production of "double-pass sinter" at less cost than when the "single-pass" was made, and the higher lead, lower sulphur, stronger sinter makes possible the production of as much lead from one blast furnace as formerly was secured from two.

A dilution of the concentrates to produce a finished sinter containing 50 to 52 per cent lead and 3 per cent sulphur gives the cheapest combined sintering and blast-furnace cost. The sulphur content of the original charge to the sintering machines is lowered without lowering the lead content by the judicious use of tailings. The openings in the grizzly bars at the discharge end of the sintering machines permit the tailings or fine sintered material to circulate in the amount desired. This fine sintered material also adds porosity to the charge and speeds up the sintering operation.

The sulphur content of the charge to the sintering machines averages 10 to 11 per cent sulphur. The first-pass sinter contains 6 per cent sulphur and the finished sinter contains 3 per cent sulphur. Enough sulphur must be left in the first-pass sinter to provide fuel to make a strong finished sinter on the second pass.

It is desired to produce for the blast furnace a self-fluxing sinter of uniform analysis and strong structure. Between the first-pass and second-pass sinter, various additions can be made to the charge—more concentrates, matte, coke breeze, sand, etc. The ignition of the sinter charge at the Herculaneum smelter is by natural gas and averages 100 cu. ft. of gas per ton of finished sinter.

With the high-lead charge, particularly on the second pass, a large amount of wind-box lead is produced from lead dripping through the grate bars of the sintering machines. In the wind box sharp-edge dividers prevent the formation of pieces of lead that are too large, and extra large doors are provided to remove the lead from the wind boxes. An increase in the silica content of the finished sinter reduces the amount of wind-box lead.

The sintering machines have been rebuilt using heavier sections everywhere and give very little trouble. Four sintering machines operating 16 hr. a day produce an average of 350 tons of double-roasted finished sinter. One 20,000-cu. ft. suction fan with 75-hp. motor is used for two sintering machines. The power used in sintering averages 12 kw-hr. per ton of finished sinter and the tonnage of finished sinter per 8-hr. man shift averages 18 tons.

Between the first-pass sintering and the finished sintering, the preroast is crushed to 80 per cent less than ⅜ in. This crushing is done in a separate crushing plant after the preroast has cooled. Crushing the preroast as part of a continuous process in double roasting creates too much dust, gives irregular crushing and moisturing of the preroast, does not allow adjustments in the charge to the finish roasting machines and runs up the cost of crushing and maintaining crushers, conveyors, etc. The preroast sinter at the Herculaneum smelter is quenched with water, put into 50-ton steel cars, unloaded and crushed to ⅜ in. in a separate crushing plant, loaded into 50-ton wooden A-dump cars and hauled back to the mixing room. The preroast crushing equipment consists of a 24 by 16-in. jaw crusher, a set of 42 by 16-in. rolls and a revolving screen. Two men crush, size and load 375 tons in 6 hr. A typical analysis of finished sinter is: Pb, 51.8 per cent; Cu, 0.80; insoluble, 10.6; SiO_2, 8.2; FeO, 15.1; CaO, 3.2; S, 2.8; Zn, 5.5.

BLAST FURNACE

The sintering machines are operated to keep sintered material just ahead of the blast furnace. The moist sintered material is not strong at any time, and tends to break up if held in storage more than three or four days. The second-pass sinter is unloaded at the blast-furnace supply bins and constitutes the bulk of the charge to the blast furnace. Other bins contain coke, wind-box lead, slag and forehearth cuttings, gravel, limestone, iron cinder and iron scale. The sinter cannot be held exactly self-fluxing, so small additions of the various fluxes are added to produce the slag desired.

The coke used is a good grade of metallurgical coke of the following analysis: H_2O, 2.5; volatile matter, 1.2; ash, 7.7; fixed carbon, 91.1.

Iron cinder is used at times to make a free-running slag when the lime-magnesia content of the zincky slag is too high. Iron scale is the cheapest source of iron and has some small reduction value in the blast furnace. Scrap iron is the most expensive form of iron flux and is used sparingly to keep lead out of the small quantity of matte produced.

The charge is gathered from bins by a larry car that carries its own scale on which each part of the charge is weighed separately. The coke is weighed first, then the fluxes and finally the sintered ore and slag. The larry car then carries its charge to the blast-furnace charge car and dumps it. The distribution of the coke is checked to prevent one side or one end of the furnace from getting more than its share of coke. To overcome irregular coke distribution, and to brighten dull tuyeres, a small amount of coke is withheld from the charge in the larry car and added by hand at the proper place in the blast-furnace charge car.

The blast furnaces are 50 in. wide at the tuyeres, 192 in. long and 20 ft. from the feed floor to the tuyere line. One furnace produces 130 tons of refined lead per 24 hr., using 6000 cu. ft. of air at 18-oz. pressure at the tuyeres. The charge column is held 12½ ft. from the feed floor after dumping the charge, giving a 7½-ft. column. The lead in the slag varies between 1.5 and 2 per cent.

The furnace puts through 32 charges in 8 hr., made up as follows: sinter, 6500 lb.; drosses, 1000 lb.; iron scale, 100 lb.; slag, 1200 lb.; coke, 650 lb.; iron cinder and gravel as needed.

The blast-furnace operation at Herculaneum varies from normal practice in the small amount of coke used and the short column and low blast pressure. The reduction can be maintained easily by a small difference in the height of the furnace column or a small increase in the lime-silica ratio. The best furnace conditions and speed are secured when a slag containing 1.75 per cent lead is made. As over one-half of the granulated slag is returned to the sintering plant to dilute the concentrates before sintering, each car of granulated slag is analyzed and the slag highest in lead is returned to the circuit. With this slag arrangement and a tight baghouse, it is easy to maintain a high lead extraction for the plant. In fact, for the last 10 years the plant recovery from lead in concentrates received from the mills to pig lead has averaged over 97.5 per cent.

A very small amount of matte is produced, varying from none to 3 per cent matte fall. The matte contains nickel and cobalt. If the furnace reduction is too strong, a fluid dross appears on the lead in the refinery and the finished pig lead is high in nickel.

A rather complete top barring every two weeks removes wall accretions. The furnace top is dropped to 15 ft. from the feed floor late on the night shift and several small dynamite bombs are shot, to free the furnace of its heaviest accretions. The top of the charge is then dropped almost to the tuyere line, coke put into the furnace and accretions barred and shot until the shaft is clean. This operation takes from 3 to 4 hr. Detachable hollow points made from old boiler tubes are driven into the crusts by a pipe and air hammer. The points and pipe are filled with water and a special bomb containing ⅓ stick of dynamite is lowered into the water-filled point. These light shots materially speed the barring operation.

Typical slag and matte analyses are as follows:

	Pb	Cu	SiO_2	FeO	CaO	MgO	S	Zn	Al_2O_3	NiCo
Slag......	1.60	0.31	26.8	36.8	8.1	4.9	3.0	10.0	5.7	
Matte....	15.10	11.1		23.9			19.8	8.5		2.6

The blast-furnace top is generally hot. The furnace gases are mixed with the gases from sintering machines, all of which then pass through the baghouse. The life of woolen bags is four years on this mixture of gases and a clear stack is maintained without difficulty. The stack is 350 ft. high and the smoke causes no damage in a farming community.

Refinery

The refining operation is very simple. To produce chemical lead, the blast-furnace lead is drossed, cooled by spraying the lead in the kettle with water, drossed again, cooled until the lead is almost frozen. The repeated drossing removes all impurities from the lead except 0.06 per cent copper, 0.01 per cent nickel and 2 oz. of silver per ton. Common lead is made by partly removing the silver, copper and nickel from the lead by the Parkes process, and corroding lead is made by a complete removal of all impurities by the Parkes process to give a lead purity of 99.997 per cent lead. There is no arsenic, antimony or bismuth in the ore at Herculaneum.

Modern Conditions

The Herculaneum smelter of the St. Joseph Lead Co. is modern and fully equipped with labor-saving machinery. Great emphasis is placed on preventing lead colic. The Missouri law on the subject is carried out in detail and then extra precautions are taken. The result is that only a few very minor cases of lead colic have occurred in the past 10 years. In the hot Missouri climate the double-sintering, blast-furnace procedure with first-class equipment allows the employment of a better class of workmen, gives better health conditions around the plant and, especially on large tonnages, gives a low cost per ton of concentrates smelted. This is particularly true when the tonnage of flotation concentrates increases as compared to table concentrates.

Smelting in the Lead Blast Furnace

By G. L. Oldright* and Virgil Miller,† Members A.I.M.E.

It is well known in metallurgical circles, though less recognized in the technical press, that there have been remarkable increases in the capacity of the blast furnace in the last five years. In places this capacity has been almost doubled. This paper will brief the experimental work carried on during more than five years with the direct assistance of the technical staffs of three lead smelters treating three distinctive types of feed. The first is the custom smelter of the International Smelting and Refining Co. at Tooele, Utah[1], with a multiplicity of ores; the second, the Kellogg, Idaho, smelter of the Bunker Hill and Sullivan Mining and Concentrating Co.[2], treating an exceedingly rich lead charge, such as is now being made more and more as the practice of concentration is improved; and the third, the smelter at Trail, B. C., owned by the Consolidated Mining and Smelting Company of Canada, Limited[3], which treats highly zinciferous charges and later recovers zinc from the slag. In comparing operations at these three smelters it must be clearly recognized that the objectives in smelting differ through differences in economics. Many operations are not, then, strictly comparable. There have also been decided improvements in operation since all of the smelters were examined, though this was but a relatively short time ago. The general factors that govern speed in smelting and the loss of metals in the smelters examined will be stressed. (For details of operation the reader is referred to the original papers.) This paper will then be an examination of the fundamentals of operating units in a search for improvements, and not a description of three great lead smelters.

Capacity of Blast Furnace

Assuming a well prepared and self-fluxing charge to start with, enough coke must be added: (1) to melt the charge, particularly the slag-forming

---

Manuscript received at the office of the Institute Aug. 24, 1936. Published by permission of the Director, U. S. Bureau of Mines.

* Supervising Engineer, Lead and Zinc Section, Metallurgical Division, U. S. Bureau of Mines, Salt Lake, Utah.

† Associate Metallurgist, Metallurgical Division, U. S. Bureau of Mines, Salt Lake, Utah.

[1] G. L. Oldright and V. Miller: U. S. Bur. Mines *R.I.* 2954, 2957, 2963, 2965 and 2966 (1929).

[2] G. L. Oldright and V. Miller: U. S. Bur. Mines *R.I.* 3088, 3094, 3095 and 3096 (1931) and 3183 (1932).

[3] G. L. Oldright and V. Miller: U. S. Bur. Mines *R.I.* 3242, 3243, 3244, 3245, 3246 and 3264 (1934).

ingredients, (2) to furnish sufficient heat for the chemical reactions of reduction, (3) to hold the charge open to allow air to penetrate it, and (4) to allow lead to liquate from the molten slag. Coke is the only infusible constituent in the charge of the blast furnace. Its removal is the slowest. The rate of burning of coke determines the rate of smelting, assuming that enough coke is added for requirements. Any amount of coke added in excess of these requirements cuts down the rate of smelting. The maximum rate of smelting depends upon the kind of charge, the proper proportioning of the ingredients, including coke, the preparation of the charge to get air through, the altering or removal of difficultly fusible compounds (ZnS, for example), and the even distribution of maximum volume of air feasible to the furnace. There is, of course, a volume of air to the furnace that cannot be exceeded for mechanical reasons. With steadily improving quality of the charge, however, it has been possible to increase steadily the volume of air to the blast furnace and even to decrease the percentage of dust made at the same time.

Experimental data on methods of preparation of the charge for the blast furnace, as done in the operation of double sintering, were obtained at two plants—Kellogg and Trail.

The feed is important; particularly the sudden variations in the chemical composition of the size of the feed. The material received on each pallet must be sintered—not some "average feed." To show the sharp variations in the composition of the feed, it is necessary to compare consecutively taken samples. The data selected for the second roast machines (from *R.I.* 3183, p. 16) show the variations in feed in 10 consecutively taken samples, sample 8, however, being omitted. The data to show the variations in feed of the first roast were selected (from *R.I.* 3243, p. 13), where 15 consecutive pallets were sampled (Table 1).

TABLE 1.—*Variation in Feed Composition According to Sieve Size*

Material	Limits of Chemical Composition, Per Cent						Limits of Size of Two Sizes as Received on Pallets, Per Cent	
	Pb	Fe	Insol.	CaO	S	Zn	Plus ½ In.	Minus 20 Mesh
Feed to second roast at Kellogg.	50.4 to 52.4	10.2 to 12.3	6.7 to 8.6	5.6 to 8.7	6.5 to 8.0	2.7 to 3.6	0 to 16.3	8.9 to 24.6
Feed to first roast at Trail.	37.2 to 45.0	12.3 to 14.7	7.2 to 12.1	2.8 to 3.6	9.6 to 10.9	9.1 to 10.8	21.0 to 44.2	7.3 to 18.3

The great variations in particle size are largely due to the difference in degree of "balling" of the fine-grained ingredients of the charge, such as galena flotation concentrates and zinc-plant residues. If screened

TABLE 2.—*Chemical Analysis and Sieve Test of Sintered Products*

Product	Depth of Layer from Top of Cake, In.	Chemical Analysis, Per Cent					
		Pb	Zn	SiO_2	Fe	CaO	S
Feed to first roast	½ from top	50.4	4.3	8.4	9.2	2.5	13.9
	½–1½	46.8	4.3	9.0	10.2	3.5	13.2
	1½–2½	42.2	4.1	10.8	10.9	4.6	11.9
	2½–3½	41.4	3.9	9.8	11.5	5.6	10.9
	3½–4½	42.8	3.9	9.2	11.0	5.9	11.4
Sinter from first roast	0–1	50.2	4.4	9.7	12.1	3.8	6.3
	1–2	49.6	4.4	11.8	13.9	4.2	5.8
	2–3	47.3	4.2	12.1	15.1	4.7	6.0
	3–4	49.8	3.8	10.0	12.0	5.6	6.4
Feed to second roast	0–½	49.6	3.6	8.2	10.0	6.2	7.5
	½–1½	49.4	3.7	8.0	10.9	5.8	7.2
	1½–2½	48.0	3.9	8.8	11.1	5.8	6.6
	2½–3½	47.6	3.8	8.6	11.5	6.4	6.4
	3½–4½	48.8	3.8	7.8	10.6	6.2	6.6
Sinter from second roast	0–1	47.4	4.5	9.6	12.3	7.3	2.3
	1–2	49.4	4.1	9.4	11.6	7.5	2.3
	2–3	47.6	4.5	9.4	12.5	7.5	2.3
	3–4	50.8	4.1	10.0	10.5	7.2	2.8

SCREEN ANALYSES OF HORIZONTAL LAYERS, FEED TO SECOND ROAST IN PER CENT BY WEIGHT OF TOTAL MATERIAL

	Layers, Inches from Top of Cake				
Screen Size	0–½	½–1½	1½–2½	2½–3½	3½–4½
Plus 0.371 in.	none	none	none	7.0	32.3
Minus 0.371 in. plus 8 mesh	16.9	15.3	56.6	78.9	54.7
Minus 8 mesh plus 48 mesh	56.4	64.5	35.0	14.1	13.0
Minus 48 mesh	26.7	20.2	8.4	none	none
	100.0	100.0	100.0	100.0	100.0

wet, about 90 per cent of the original constituents at Trail and some 70 per cent of the charge at Kellogg would pass 200 mesh. The coarser materials are crushed limerock and siliceous or coarser lead ores, and at Kellogg some jig and table concentrates are also received. In considering variations, it is to be remembered that: (1) enough sulphur as fuel has to be supplied in the sinter, both to ignite and to remove the sulphur, and (2) a final hard cake must be left. The two objectives often conflict.

The maximum variation in fuel content noted above was $\frac{8.0 - 6.5}{8}$ or 18.8 per cent. The variation in fusible constituents is also notable. In general, the feed to the second roast is much less variable in composition than is the feed to the first; the first roasting operation not only removes much sulphur and dries the charge but also mixes the ingredients better.

Besides the variations from pallet to pallet, the particles in the first roast are also semiclassified on each pallet as to particle size and weight by rolling with varying degrees of freedom down inclines from the swinging chute. The coarser, heavier particles near the bottom of the pallet are usually richer in lead than in the center of the cake; much of the lead fines stays near the top. When the first roast is recrushed and rebedded for the second roast, there is the same tendency to form layers of varying compositions. A bedding system for the feed to the second roast would be expected to make the chemical composition of the charge from pallet to pallet much more uniform, but variations from top to bottom of the cake will be found unless the feed to the first roast is better mixed.

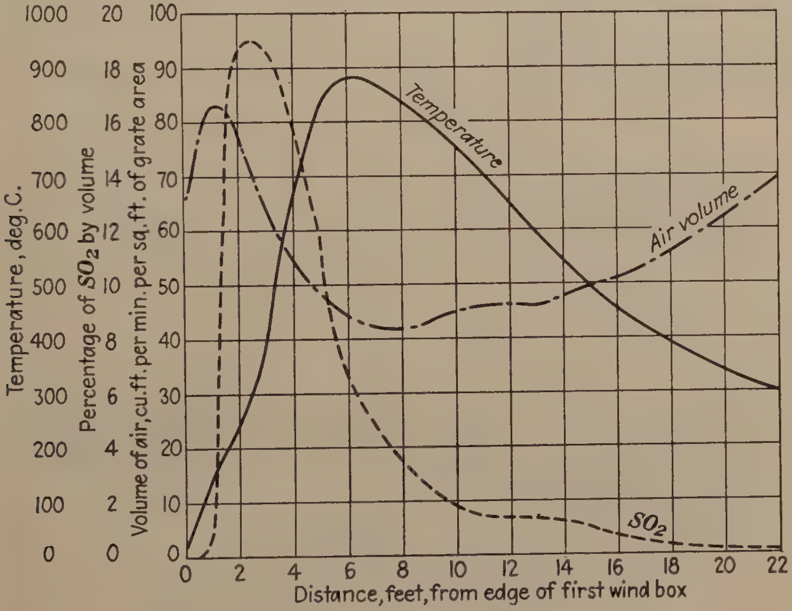


FIG. 1.—GASES IN FINAL ROAST, KELLOGG, IDAHO.

To learn the variation in feed to the Dwight and Lloyd machines, and also the change in composition of the sinter cake, the material was sampled by cutting horizontal layers across the pallets. Table 2 gives the chemical and sieve analyses of such products at Kellogg. The sets of samples are for different days and are not of the same materials.

The curves of Figs. 1 and 2 give the volumes of gases going through the cake, their SO_2 content, and temperature of the cake, as the pallet travels across the wind boxes. The samples of SO_2 gas at Kellogg were taken under the center of the pallet. At Trail they were taken likewise. The following curves showing SO_2 concentrations, air volumes through the sinter cake, and temperatures are the averaged results and show the general trend of sintering. The separate cakes, however, ignited and burned at different rates. If plotted for any one test the curves show the same shape but vary in magnitude. The sintering machine operates at a constant draft. The volume of gas through any given spot in the cake then obeys the laws of shunts—any crack or abnormal porosity of the cake admits far more than its proportion of air. Usually, but not always, the SO_2 concentration varies somewhat inversely as the volume of air. A faster rate of burning, or cooling, may result with added volume of air and may increase or decrease the concentration of SO_2.

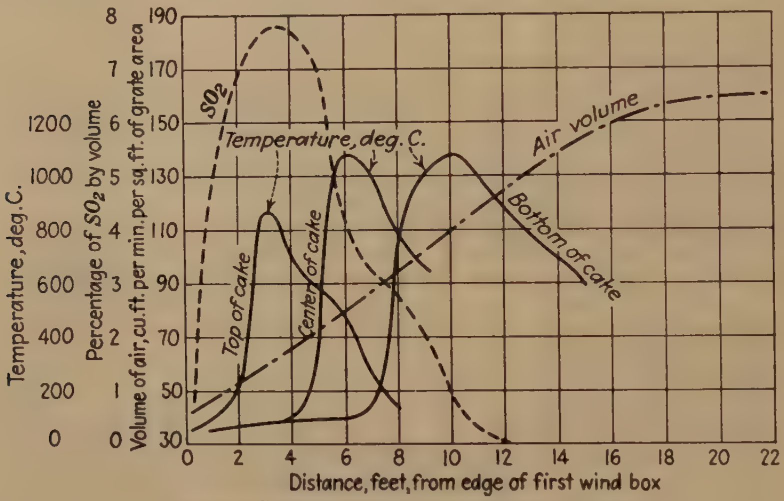


FIG. 2.—GASES IN FINAL ROAST, TRAIL, B. C.

The richness of the lead charge at Kellogg is exhibited in the richness of the SO_2 gas made by the "roast-reactions" between oxidized lead compounds and lead sulphide; metallic lead is the other product of the reaction. As those operating the Scotch hearth have found, the addition of inert diluents greatly reduces the speed of the reaction; the direct contact of the reactants in a semiliquid state seems essential for much metallic lead (and SO_2) to be made by the reaction. The great differences in air volumes follow from the causes of evolution of SO_2 of varying richness—just before SO_2 of the maximum strength is evolved from a semiplastic cake at Kellogg, the volume of air through the cake starts to drop sharply, and does not increase much until the sintering operation is about half over. At Trail, the volume of air through the cake increases gradually during the second roast.

A special pallet was made to draw off all the gas completely across one section of the pallet, as shown in Fig. 3.

The results, when plotted, showed the same trend as the SO_2 concentration curves of gases taken at a single point. The average percentages, however, were slightly less, as the sample includes the poorer gases at the sides of the pallet.

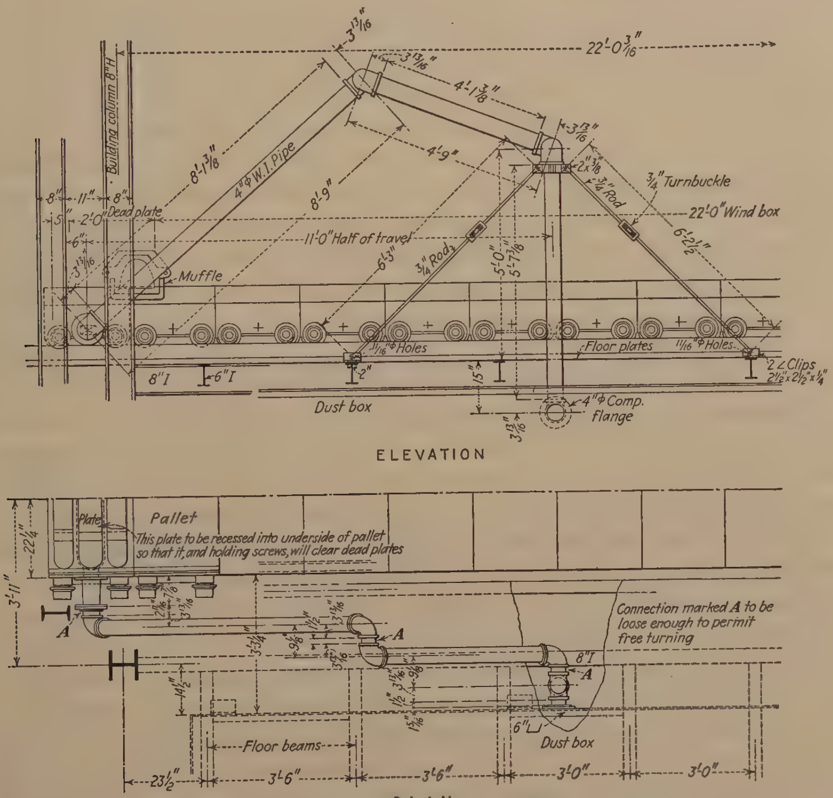


FIG. 3.—GENERAL LAYOUT OF PALLET SPECIALLY DESIGNED TO REMOVE ONLY GASES PASSING THROUGH CAKE.

EXPERIMENTS TO IMPROVE SINTERING PRACTICE

The sides of the pallet offer lines of weakness through which air may be easily sucked, particularly if coarser material is also at the sides. Extra air drawn down through the pallet acts like a sand blast to make still larger openings in the pallet gratings, so that the wearing effect is cumulative.

Attention has already been drawn to the variations in feed to the sintering machines. The feed as bedded on the pallets also varies from one side to the other. If the width of the pallet is divided into three equal sections, the average volume of air passing through each section (1 by 3 ft.) and for a distance of pallet travel of 11¼ ft. varies naturally with the feed through which the air is being measured. One test gave the average air volume for the south side as 114.1 cu. ft. per square foot of grate area per minute, the center section 47.7 cu. ft., and the opposite side 82.7 cu. ft. As the loading chute swings back and forth in normal practice, it selectively throws coarser material to the sides of the pile of feed, and more of these coarser particles then run down the pile onto the sides of the pallet. A curved deflection plate was installed, which gave a uniformly porous bed across the pallet. The feed then dropped vertically and rolled down the pile of material in a direction parallel to the line of travel to the pallet. With other variables, such as the composition and nature of the feed, first smoothed out, the manner of bedding pallets is worthy of close attention by those wishing to secure a more uniform cake, as well as to make less and richer SO_2 gas.

Optimum Bedding on Pallets According to Particle Size

The natural tendency of coarser particles to bed closer to the pallet and of fines to go to the top of the cake is useful in that coarser particles fill openings in the grate so that the fines will not run through it and the fine sulphides on the top make it easier to ignite the cake. The variation of the chemical composition of the feed of the particles of various size makes it difficult to determine just what proportion of the particles of various sizes should be in each layer. As an extreme, a batch of feed at Trail was sieved into four sizes: plus ½-in., minus ½ plus 4-mesh, minus 4 plus 8-mesh, and minus 8-mesh. These sizes were placed carefully by hand on the pallet in the order given. The top ignited quickly and burned at a high temperature before the bottom part of the cake was well ignited. The differences in rates of burning and expansion split the cake horizontally, there being 2 in. between the layers. Some fines were needed with the coarse to ignite the latter, and some coarse was needed with the fines to give porosity and allow the bottom to ignite more quickly. In practice, if feed were sieved into some four sizes as above and each bedded separately on the pallet, there would be less chance for differences in composition and sizes from pallet to pallet. Jarring of the machines would also tend to allow fines to settle between the coarse particles.

Ignition

The bedded charge on the sintering machines is usually ignited by a coke, oil, or gas flame. The size and shape of the igniters vary. One of the main variations, however, is the width of the hot zone. Before the first wind box is reached by a moving pallet it must pass over a flat metal plate some 30 in. wide. This is called a "dead plate" and acts as a seal to prevent air from entering the wind boxes from the ends instead of through the cake. The bottom of the pallets and the surface of this plate are not a perfect fit, consequently there is a slight suction of air through the cake as it passes over the dead plate. One measurement of the amount of this air is shown in Table 3.

TABLE 3.—*Volume of Air Passing through Cake*

DISTANCE FROM EDGE OF DEAD PLATE, IN.	AIR THROUGH CAKE, CU. FT. PER MIN. PER SQ. FT. GRATE AREA
0	0
6	2
18	8
24	15
30	50

Minus 20-mesh ore containing 6.5 per cent sulphur and 6.5 per cent moisture will ignite in one minute when gas is gently drawn through it at 800° C. Electrical ignition is satisfactory as long as there are fine sulphides on top of the cake, although the decrepitating sulphides cause some trouble by flying up, striking, and sticking to the wires. With coarser material on top, a penetrating flame is needed. The proper point of ignition above the dead plate is important from the basis of fuel consumption. An overly large volume of air through the cake at this point is harmful, as it may chill the gases; small volume of hot air and gas is usually enough, if the fuel is burned uniformly across the pallet. Besides the size of the particles, the content of "sulphide sulphur" and the volume of gases through the cake, the amount of moisture in the charge must be regulated to give the best rate of burning downward. The rate of flame propagation downward should be rapid, yet not so fast that the top layer will fuse, the cake split, and channels form that will allow air to escape without going through part of the cake.

Moisture in Charge

The materials with which moisture is associated were found to have a surprisingly great influence on the porosity and structure of the cake, on the rate at which the sulphide ignites and burns, and therefore on the strength of SO_2 gas that can be made on Dwight-Lloyd machines. With the rich, fusible charge obtaining at Kellogg, the metallurgists had to guard constantly against fusing the cake before the sulphur was burned off. The endeavor was to bed the feed to the second roast with the quantity of water that would give the minimum weight per unit volume. This desideratum was closely linked to obtaining a material that, when mixed with the remainder of the feed, would make a product containing a maximum quantity of water without being like mud, or dripping. Of all the smelter products freshly formed, unburned flue dust retained thus a maximum amount of water, both in itself and when admixed with the charge. At Trail, the freshly precipitated Cottrell dust was particularly efficacious in this regard. This dust weighs about 14.4 lb. per cu. ft. when fresh and 52 lb. when it has stood and oxidized somewhat. With unburned flue dust added to the second-pass sintering machines, the material as bedded weighed 125 lb. per cu. ft. and would retain 7 per cent of moisture. With the same weight of burned flue dust the bedded material weighed 135 lb. per cu. ft. and would retain only 5 per cent of moisture and still give the crumbly, nonmushy structure desired. Materials such as zinc-plant residues, containing when wet some 29 per cent of moisture and when partly dry some 19 per cent, do not give a bedded material of desirable structure or properties.

When blast-furnace practice was improved, so that much less dust was made, some approximately quantitative figures were obtained as to the difference in results in sintering. With a larger proportion of flue dust on the feed to the first roast, the second roast cake ignited and burned at such a rate that gases as rich in SO_2 as 14.5 per cent were obtained. Gas containing 11 per cent SO_2 was obtained for the first 12 ft. of pallet travel. Without the flue dust, the usual maximum strength of SO_2 gas is 4 to 7 per cent. It is not effective to add this flue dust to the second roast—the structure given to the first-roast particles persists even after crushing, and when the material is bedded and then roasted the second time. If the first sinter is not porous, it is more difficult to expose the sulphides to the air in the second roast. The sulphur content of the faster burning sinter is usually 0.7 to 1.7 per cent, and some 0.2 to 0.7 per cent lower than in the slower burning cake. The slower burning cake is usually more compact and darker, showing that it contains less iron in the ferric condition.

With the more porous structures given by more flue dust, in general as the pallets move across the wind boxes the temperature in the cake rises more quickly, and SO_2 is evolved more rapidly. In the slower burning cake the SO_2 keeps coming off for much longer. The temperature as measured by thermocouples embedded at various elevations within the slower burning cake may have a higher maximum and also be more prolonged. For the slower rate of burning, one may never get through the cake more than 100 cu. ft. of air per minute per square foot of grate area in 22 ft. of pallet travel. With the faster rate of burning 100 cu. ft. through the cake per square foot of grate area may be obtained after the first 5 ft. of pallet travel and over 200 cu. ft. before the wind boxes are traversed.

Increased capacity may be insured by speeding the rate of travel of the pallets containing the faster burning sulphides. It was shown in later experiments that by placing a thermometer under the cake near the end of the last wind box, the machines could be speeded to greater production without additional hazards to health by discharging fuming sinter cakes. A recording pyrometer also gave a check on the whole sintering operation. In short, the structure of the cake made in sintering is governed largely by the way in which the cake is prepared and the way in which it burns after it is ignited in the first 5 or 6 ft. of travel of the pallet.

Recirculation of Gases

With the faster burning sinter most of the SO_2 was removed in the first 7 ft. of travel over an 11-ft. wind box and the volume removed from the next 4 ft. of the wind box was about equal to that removed from the 7-ft. section. By placing a partition (shiftable if desired) in the wind box and circulating the gases from the second section back through the first, the gas coming off the first section would be enriched in SO_2. The experiments to enrich SO_2 gases thus were not entirely successful: slower burning sinter had to be handled, which upset all calculations. The recirculated gas contained less oxygen, but the loss of heat in the cake was more than made up by the increased heat of the oxygen. The cake fused more readily, a noteworthy point, particularly when there is a scarcity of sulphide sulphur for fuel and a plant where the air can be heated.

The solids in the Dwight-Lloyd gases were normally as shown in Table 4.

TABLE 4.—*Solids in Gas from Sintering Machines*

DISTANCE ALONG WIND BOXES, FT.	SOLIDS PER CU. FT., MG.	NATURE OF SOLIDS
3	85.6	Mostly mechanical dust
6	32.2	Less dust, more fume
9	26.4	Still less dust, much fume
15	14.6	Mostly true fume

The greater part of the solids in the gas from the 7 to 11-ft. sections was filtered out and left on top of the filter cake of the first 7-ft. section. Even when rich SO_2 gas is not desired for acidmaking and other purposes, the recirculating of gas will give a smaller volume of gases to handle, containing less dust.

Long versus Short Machines

In general operation, the increase in SO_2 concentrations and temperatures occurs in about the same manner with long and short machines, but it is more prolonged in the longer machines. With cakes of the same density, more sinter is usually produced by the shorter machine per foot of length of machine. The cake is somewhat less dense on the long machine, chiefly because the material when being bedded is jarred less by the falling of the discharging pallet. The long machine is good for drying much wet material like zinc-plant residue on the first roast. The main advantage of the long machines is that there is less overhead equipment per ton of sinter made. It is often easy to increase the length of the machines as a means of increasing the capacity of the plant.

Thin versus Thick Beds

At Trail, more sinter was produced with a thinner cake. Thus finished sinter could be made and the pallets run 18 in. per minute with a 7-in. bed compared to 9 in. of travel per minute possible for an 11-in. bed, and still good sinter be made in both instances. The slower machines, however, require less expenditure for upkeep. The presence of infusible material as zinc-plant residue helps keep a thicker bed sufficiently open for gases to pass through, and such materials have longer to dry. At Kellogg, with the more fusible charge, sinter could not be made successfully in thick beds.

FUTURE DEVELOPMENTS OF SINTERING

Metallurgists have shown their usual adaptability in being able to sinter material of widely differing ranges of composition, even when the variations have been sharp. A feed of more uniform composition would, however, seem one of the great prerequisites to further improvements. If such a feed could be given to the first-roast machines, the second roast could be more uniformly bedded as to particle size if a series of sieved products was used, and there would also be less chance for the feed to segregate in every intermediate storage bin, as at present.

Each stage of improvement in sintering practice has had some limit of sulphur content set, under which supposedly the sulphur could not be roasted off and a hard sinter cake of sufficient strength obtained to give a porous column in the blast furnace; 3.5 per cent of sulphur was once thought the lower limit. Now, with less than 1.5 per cent of sulphur in a cake at Trail, it is weak structurally; with 0.7 per cent sulphur the cake is very crumbly. It is then, perhaps, possible to feed the cake in such a way that the material contains still less weight per cubic foot and thus one can probably remove still more sulphur. The desulphurized crumbly cakes could then be agglomerated by some means, such as with coke breeze on a Dwight-Lloyd machine or in a revolving cylinder. Experiments at Kellogg showed that much of the lead in the sinter cake can be reduced to metal on the Dwight-Lloyd. Although the lead reduced on the sintering machine would not need to be reduced in the blast furnace and coke breeze is cheaper than the part of the coarse coke replaced in the blast furnace, it is difficult to liquate metallic lead from sinter cake by the use of carbon. The metallic lead present would make the charge in the blast furnace more fusible and also probably help to keep the coke there from burning rapidly. The amount of metallic lead found in the wind boxes was found to be almost proportional to the amount by which the lead content of the sinter cake exceeded 49 per cent. Metallic lead is then seemingly formed by interaction between lead sulphide and oxidized lead compounds in the liquid state;

any diluents seemingly decrease the amount of lead usually found in the wind boxes after the first few feet of travel in the second roast. For autogenous sintering following present trends, attention should be centered more on what happens in the first 6 ft. of pallet travel and in bedding a cake of a nature that will ignite, and burn through to the bottom more quickly at a higher temperature to eliminate sulphur still better and to give a better fused cake.

The well desulphurized but crumbly sinter containing about 0.7 per cent of sulphur smelts in the blast furnace much more slowly than sinter that contains 1.5 per cent or a little more of sulphur. The more sulphurous material is said to be of better quality; that is, it is harder and in larger pieces. With a charge composed entirely of sinter of good quality, most of the problems of the lead-smelting operations proper resolve themselves into a study of the even distribution of coke and still larger volumes of air to the blast furnace.

The fusible nature of lead compounds limits the richness of the feed that can be desulphurized successfully. The richest feed that was successfully sintered contained 56 per cent of lead. The operation of sintering, then, fixes at present the limit on the richness of the concentrate that can be handled in the usual scheme of treating ores by mechanical concentration, sintering and smelting, without diluting any of the concentrates made. The percentage of sulphur in the sinter cake increased at a roughly uniform rate from 0.7 to 3.5 per cent, as the lead content of the sinter increased from some 47 to 56 per cent.

General Chemistry of Smelting in the Blast Furnace

The reducing power of the blast-furnace gases might be considered in terms of producer-gas reaction, $CO_2 + C = 2CO$. The rate of reduction of oxides with solid carbon is relatively slow; therefore the combination of carbon with atmospheric oxygen would be important chiefly for its heat-making properties and the production of carbonaceous gases. The concentration of carbon monoxide in the above equilibrium increases sharply from some 10 per cent at 550° C. to about 90 per cent at 800°. Practically all blast-furnace slags must be heated above 1000° C. to melt them. At this temperature the carbonaceous gases in contact with an excess of coke are almost entirely carbon monoxide. When air is blown into a bed of fine coke alone on a grate using natural draft, the oxygen penetrates some 3 or 4 in. into the bed of coke before being transformed entirely to carbonaceous plus inert gases. With a high blast pressure, say of 20 lb. or less, as in the iron blast furnace, the oxygen may penetrate some 30 in. into the charge column, with its relatively coarse coke and ore. Possibly some of the coke is blown away from the tuyeres mechanically, and some time is also needed to heat the air to reaction temperature.

There are, then, three zones of combustion in the iron blast furnace—a somewhat pear-shaped zone in which oxygen is not entirely absent, a zone that contains mixed carbon monoxide and dioxide and, as the column of coke is penetrated farther, a zone that contains only carbon monoxide and inert gases. In the iron blast furnace there is about 40 per cent of coke to the rest of the charge, and in the lead blast furnaces examined less than 14 per cent.

In studying the rate of combustion in the lead blast furnace there comes up at once the matter of the irregular arrival of coke at the tuyere zone, and the irregularity in the volume of air coming in through the tuyeres, as well as the composition of the solid charge to be reduced and smelted. For the relative volumes concerned it may be noted that about three tons of slag was made per ton of lead at Tooele and one ton of lead per ton of slag at Kellogg. About 0.5 ton of slag is made per ton of iron in the iron blast furnace. The relative volumes of the oxidized ingredients of the charges and coke, the light weight of the coke, and its great volume, are to be noted. Thus in an iron blast furnace the charge after mixing appears to be chiefly coke; the corresponding lead blast-furnace charge appears to be chiefly sinter.

When any gas within a furnace contains more than the percentage of nitrogen in the air (79.2 parts of nitrogen against 20.8 parts of oxygen), oxygen is being extracted from the blast by some of the metallic ingredients of the charge. The maximum concentration of carbon monoxide that can result from burning carbon with air alone is attained when the 20.8 parts of oxygen go to twice that number of volumes of carbon monoxide. This would give $(20.8 \times 2)/(20.8 \times 2 + 79.2) =$ 34.4 per cent of carbon monoxide. By difference, 65.6 parts of nitrogen would be present in such a gas. Should any gas contain less than this proportion of nitrogen, it is taking up oxygen from the solid ingredients of the charge.

In regard to the solid constituents of the charge, the blast furnace handling raw feed will, of course, have to perform many of those preliminary functions of dehydration, removal of carbon dioxide, some oxygen and sulphur, and also part of the slagging operations themselves, that are done elsewhere on the sintering machines. Where a blast furnace is smelting what may be called "slag sinter" (that is, all the sinter is as a slag instead of a poorly consolidated conglomerate, such as material that has only been given an oxidizing roast appears) the blast furnace has little more to do than melt the charge and to liquate the metallic lead from the molten slag. The iron in well prepared sinter is largely in the ferrous state—it was found difficult to determine by wet methods just what portion of the iron was in the ferric state, although the point is of considerable importance. For the reduction of the lead itself, Table 5 gives a general picture of the compounds present.

TABLE 5.—*Lead Compounds in Sinter of Final Roast*

	Total Lead Content, Per Cent	Percentage of Total Lead as			
		Metal	Oxide	Sulphide	Silicate
Kellogg	46.2	9.3	58.5	24.4	7.8
Trail	37.6	7.7	66.0	16.9	9.4

In a special Kellogg sinter prepared with coke, 75 per cent of the total lead was present as metal, 8.3 as silicate plus oxide, and 16.7 as sulphide.

As will be noted later, the zinc that is not volatilized is largely carried out in the slag as zinc oxide in solution in ferrous silicate. The zinc, then, is in the same form as it was in the sinter, if the sinter was a true slag, except possibly some zinc that entered the furnace either as a sulphate or sulphide. For the form of combination of sulphur in well roasted sinter cake, at Kellogg it was found that about 0.1 to 0.4 per cent of sulphur was combined as lead sulphate, 0.4 to 0.6 per cent as calcium sulphate, and around one per cent largely as lead sulphide. The lead sulphide was dispersed through the sinter cake so finely that it could not be identified with the microscope. Except the larger pieces of limestone, the lime in the charge is the oxide or combined with silica.

For the amount of reduction necessary in the blast furnace, the literature shows that oxidized lead compounds are reduced by carbon monoxide to metals at a few hundred degrees centigrade: 650° C. was the temperature given for the most fusible of the silicates. If necessary to replace lead from its sulphide combination with metallic iron, it may be noted that at 1000° C., 70 per cent CO and 30 per cent CO_2 are in equilibrium FeO and Fe. Where scrap iron is added as standard practice, it would not be necessary to reduce iron to the metallic state in the blast furnace. Thus for the reducing power of carbon monoxide on zinc oxide at 1027° C., 15.9 per cent CO_2 and 68.1 per cent CO are in equilibrium with zinc vapor at a total pressure of one atmosphere. At 1327° C. the figures are 40.2 per cent CO_2 and 19.6 per cent CO. (The pressure of the zinc vapor in both cases was the same as that of the carbon dioxide.) At the equilibrium conditions between 1000° and 1400° C. (the temperature range usually obtaining at the smelting zone) the lead, zinc, and iron oxides in the charge would metallize, provided that these were sufficiently freed from combination with other radicals.

The conditions actually obtaining within the blast furnace were found to be more a function of rates as determined by the various variables of operation than of equilibrium conditions. In considering the samples of gases taken from the tuyeres it should be remembered that these were taken through ⅛-in. water-cooled sampling pipes, and that during this time coke, gas, and charge were moving past the pipe at varying rates of speed. The samples taken are then composites of a large number of samples during varying operating conditions, although they were taken during a short interval.

When the experimental data were gathered, the smelter at Tooele had 75 per cent of sinter on its charge containing about 24 per cent of lead, Kellogg 85 per cent of sinter containing 45 per cent of lead, and Trail about 85 per cent of sinter containing 37 per cent of lead.

EXPERIMENTAL DATA ON CONDITIONS OBTAINING IN THE LEAD BLAST FURNACE

The data in Table 6 give the average compositions of gases obtaining on a vertical plane, taken midway between the side walls of the blast furnace at the tuyeres and at the top of the charge. They may be compared with what has been said as to the compositions of gases obtaining under conditions of equilibrium, particularly the ratios between the quantities of carbon monoxide and dioxide present.

TABLE 6.—*Average Analyses of Samples Taken at Vertical Plane Midway between Side Walls of Furnace*

Plant	*Zinc* in Slag, Per Cent	Volumes O_2[a] Extracted from Charge		Percentage Total Oxygen[c] from Charge		Analyses of Gases and Total Oxygen Equivalent, Per Cent									
						Top					Tuyeres				
		Top	Tuyere	Top	Tuyere	CO_2	CO	O_2	N_2	Total[d] O_2	CO_2	CO	O_2	N_2	Total O_2
Trail....	18.0	4.4[b]	2.4	18.5	11.3	17.2	5.1	4.0	73.7	23.8	10.5	13.8	3.9	71.8	21.3
Kellogg.	9.5	6.3	10.3	25.3	39.7	18.2	8.4	2.5	70.9	24.9	11.5	28.7	0.1	59.7	26.0
Tooele...	5.5	6.6	19.2	27.7	59.9	12.0	21.6	1.0	65.4	23.8	12.5	38.0	0.6	48.9	32.1

[a] Volumes equivalent O_2 extracted from charge per 100 volumes of gas at top and tuyeres.

[b] Sample calculation: Analysis of top gas and "total equivalent oxygen" are given. Neglecting nitrogen (less than one per cent) in coke, the volume of oxygen in air (20.8 per cent O_2 and 79.2 per cent N_2) combined with the 73.7 volumes of nitrogen in the top gas is then 20.8/79.2 × 73.7 or 19.4. The difference between the 23.8 volumes of "equivalent oxygen" present and 19.4 volumes derived from air, or 4.4 volumes of O_2 were then extracted from the charge.

[c] Percentage of total equivalent oxygen in gas at top and tuyeres derived from charge. Total equivalent oxygen = volumes oxygen needed to form volumes of all gases, or percentages by volume $CO_2 + O_2 + \frac{1}{2}CO$. (Hydrogen and SO_2 disregarded.)

[d] Total O_2 equivalents.

Across the furnace from one tuyere to the other, at the tuyere zone conditions differ greatly at the various lead smelters, and these in turn differ from conditions in iron blast furnaces. It may be said for all lead smelters that there is no zone of coke at the tuyeres large enough to prevent completely the presence of carbon dioxide, although at times the percentage of carbon monoxide may be rather high. In general, there is even a little oxygen present. The tuyere zone at Tooele most closely approximated that of the iron blast furnace. Running in from the tuyeres there was a zone in which oxygen was being consumed rapidly, and then a fairly loose zone was encountered in which molten ingredients of the charge were flowing freely. A third zone was next met in which there was a considerable accumulation of coke and a much smaller portion of free-flowing molten charge. The carbon monoxide in this last zone was fairly rich.

At Kellogg there was usually a thicker accumulation of semiplastic charge near the sides of the furnace, and the total smelting area was usually 25 to 60 per cent of the whole area at the tuyere zone. This smelting area was exceedingly irregular and also contained various "islands" of unfused material. The openings through this semiplastic area near the side walls of the furnace acted as prolongations of the tuyeres themselves and served only to preheat the blast; in fact, considerable lead was burned by the air stream in traversing this area. After the air had passed this semiplastic area, the change to a gas containing high percentages (some 80) of carbon monoxide was at times abrupt. On one sample it was estimated that over 90 per cent of the total equivalent oxygen present had come from the solid charge, in contrast to the fact that oxygen was being extracted from the blast while it traversed the plastic portion of the charge near the side walls.

At Trail, as at Tooele, there was also considerable oxidizing of the charge near the side walls of the furnace, and then a reducing zone nearer the center line. It was noteworthy at Trail that the composition of the gases at the tuyere zone was about the same with 10 or even 16 per cent of coke on the charge. During the experiment more than one furnace was always running, and these were connected with a simple direct header. With the greater percentage of coke, a more open charge column was obtained and more air passed through the furnace. To make statements on the composition of the gases as a function of the amount of coke added, the amount of either coke or air would have to remain constant. At Tooele, oxygen was nearly always extracted from the charge and only occasionally was the percentage of nitrogen in samples taken greater than that in air. To make suggestions as to relative speeds of reaction in the furnaces one should consider the volumes of gases reacting, as well as their noted analyses.

The extreme temperatures at the tuyere zones at all three plants showed about the same range—from about 1000° to 1400° C. The average temperatures, however, varied considerably, as did the point of the maximum temperature at the central plane of the tuyere zone. At both Trail and Kellogg, with their higher percentages of sinter, the maximum temperatures at this place might be anywhere from near the slag tap to the back of the furnace. At Tooele, the temperature was highest towards the slag-tap end of the furnace and dropped from some 1360° to 1040° C. at the back. The corresponding rate of smelting as measured by the rate of subsidence of the charge was at the maximum where the temperature was highest. The blast pressures at the three plants are shown in Table 8. It is to be remembered that the pressure is more a measure of the resistance of the charge column than of the volume of air put through. The volume of air blown into the furnaces as measured by the revolutions of the blowers was about constant at all plants—5000 cu. ft. per minute. At Kellogg, 7500 cu. ft. was used at times, and it is also possible that at Tooele when operating only one blast furnace the volume of air was considerably higher than when two furnaces were operated from the same main.

The volume of air through the various tuyeres was measured for only one plant—Kellogg. The volume of air through any one tuyere when not entirely plugged varied from 130 to 600 cu. ft. per minute. Punching the tuyeres made but surprisingly little difference upon the volume of air admitted to the furnace. The same was true of the other ordinary variables of operation. During a period of about ½ hr. the volume through any one tuyere not entirely closed usually varied only a few per cent. Over a period of a few days this volume might vary several times. In other words, the amount of air passing through any given tuyere was more a function of the porosity of the charge above the tuyere level than it was of the degree to which the tuyere itself was open.

At the time of the experiment, the smelter at Tooele used the least sinter on the charge, somewhat more coarse limerock, and also scrap iron in relatively large pieces, all of which would make for irregularities in rates of smelting. It has been mentioned that the smelting was most rapid at Tooele towards the slag tap and where the temperatures were highest. The slag taken from the various tuyeres also showed marked differences, each composition depending upon the temperature obtaining. Thus at the hottest zone of the furnace the slags were richest in lime. The form of combination of lead in the slag from each tuyere, however, differed not only with the temperature obtaining at that tuyere but also with the speed of smelting. The percentage of carbon monoxide at any given tuyere, like the rate of smelting, increased with the temperature. Where the charge flowed most rapidly past the tuyere zone, toward the center of the furnace, the amount of lead in the silicate form increased greatly. Although the percentage of carbon monoxide present was great and that required to reduce lead silicate under equilibrium conditions is low, considerable time is needed for the reduction of lead silicate. As will be noted later, when the capacity of a blast furnace is speeded up, there is often an increase in the amount of lead in the slag in the silicate form. Another result of varying temperatures at the tuyere zone was that on tapping slags there was a marked lowering in the carbon monoxide content of gases taken from the tuyeres near the slag tap. The removal of a large volume of hot slag in a short time lowered the temperature and caused corresponding changes in the composition of the carbonaceous gases.

TOP GASES FROM THE LEAD BLAST FURNACE

The detailed data on gases from 21 equally spaced areas on the surfaces of the charges at the three smelters were averaged, assuming that the gases came up through the charge at a uniform rate (Table 7). (This is not a true assumption because the gases come off in largest volumes from near the center of the furnace and these gases are poorest in oxygen. All furnaces have about the same variables in operation, however, so the averaged figures are roughly comparable.)

TABLE 7.—*Analysis of Top Gas at Certain Heights above Tuyeres*

Plant	Analysis of Top Gases, Per Cent by Volume			Coke on Charge, Per Cent	Height of Charge Column above Tuyeres, Ft.
	CO_2	O_2	CO		
Tooele[a]	13.6	1.3	19.2	13.5 (ave.)	15
Kellogg	14.3	2.2	12.5	9.5 to 12	9
Trail	15.9	4.8	5.1	10 to 11	13

[a] At Tooele more CO_2 is calcined from raw limerock fed to furnaces.

The greater reducing power of the gases in the tuyere zone at Tooele over those at Kellogg and Trail persists to the top gases. Table 6 gives some approximations showing the percentages of oxygen removed from the charge at the three smelters, and particularly the effect of large amounts of zinc in the charge upon the percentage of the oxygen burned by the solid ingredients of the charge. When zinc burns at the tuyeres, the zone of greatest reduction tends to move higher up the shaft of the furnace, and the greater the percentage of the zinc in the charge, the greater the tendency to reduce to metal. Thus it is found, in the furnace for volatilizing zinc from slags at Trail, that the zinc volatilizes at an approximately even rate from slags containing 17 to 7 per cent of zinc, after which the rate slows down greatly. With the weaker conditions for reducing and volatilizing in the blast furnace, the slags can contain more zinc before the rate of volatilization becomes appreciable.

The average temperature of the gases at the top of the furnace does not have much significance, since the temperatures vary from 100° or so to those obtained at the tuyere zone. The hottest spots, of course, carry far more than their proportion of dust. The furnace with the hottest top tends towards making the greatest amount of dust (Table 8). It seems probable that more flue dust would be made at Trail if the charge column were as short as that at Kellogg. As the figures stand, however, the amounts of flue dust made are greatest where the temperatures of the top gases are the highest.

TABLE 8.—*Dust Made and Top Temperatures*

Plant	Tons of Flue Dust per Furnace Day	Charge Column		Size of Furnace, In.		Air Used	
		Average Temperature at Surface, Deg. C.	Height, Ft.	Tuyere Section	Top Section	Pressure, In.	Approximate Volume, Cu. Ft. per Min.
Tooele......	1.5	159	15	54 × 180	80 × 180	42	5000
Trail.......	9.8	298	13	48 × 180	84 × 180	36	5000
Kellogg.....	11.0	507	9	48 × 180	80 × 180	24	5000–7500

In smelting pyritic copper ores in the blast furnace, the attempt was made to use the furnace in part as a blast roaster, and to utilize in smelting the charge the heat evolved from burning the sulphides at the tuyere zone, so that it would be necessary to use as little coke as possible. (Coke was probably needed more to furnish carbon monoxide to reduce Fe_3O_4 at a low temperature than to furnish heat units.) By diminishing the percentage of coke on the charge, the lead blast furnace also may be made in part to act as a blast roaster, although the percentage of the sulphur burned at the tuyere zone will be considerably a function of the percentage of the sulphur in the charge (Table 9). It is suggestive to contemplate to what extent the blast furnace could be used as blast roaster with lead as well as with more infusible copper ores. The experience of those using the Scotch hearth would indicate that among the problems would be to operate the furnace with a cool top to avoid excessive losses by volatilization, and to get air through a charge fused to varying degrees.

TABLE 9.—*Removal of SO_2 in the Lead Blast Furnace*

Plant	Approximate SO_2 Content of Top Gas, Per Cent	Usual Coke in Charge, Per Cent	Approximate Percentage of Total Sulphur in Feed Removed by Blast Furnace	Remarks
Tooele... ..	0.005 to 0.018	13.5	Small	Matte made.
Kellogg.....	0.08 to 6.05[a]	9.5 to 12	About ⅔	O_2 low midway between tuyeres; elsewhere high.
Trail........	0.018 to 1.22	10 to 11	About ¼	Lowest percentage of sulphide sulphur in feed.

[a] Average about 1.5.

ACCRETIONS

The amounts of sulphur and coke present in the blast-furnace charge and quantity of matte made determine the amount of formation of the more troublesome, deeply seated variety of accretions.

A furnace using a low percentage of coke has been seen to act partly as a blast roaster and also to have a smaller free-smelting area at the tuyere zone. The semiplastic materials surrounding the sides of the free tuyere zones under these conditions may consist rather largely of constituents of the charge. In the furnace containing more sulphides and using more coke, these accretions will be largely sulphides. In their extension upward towards the top of the smelting column, the accretions will still contain sulphides, although as the temperature drops these will be infiltrated to some extent by the more fusible constituents of the charge. The length of a furnace campaign is usually governed by the rate of accumulation of sulphide accretions in the crucible, these building downward from the surface of the lead bath. When the connecting channel between the lead well and the molten charge within the blast furnace can no longer be maintained without an excessive amount of labor, the furnace is closed down and the crucible is cleaned. The sulphides of copper and of zinc are particularly effective in forming accretions. Lead sulphide is also found. The deeper seated accretions somewhat above the tuyeres are also sometimes effective in blocking off supplies of coke to the tuyere zone. They thus exaggerate those fluctuations of temperature that cause them to be formed in the first place.

With less sulphur and coke in the charge, a different type of accretion is formed, largely by material that is volatilized or carried in the gas stream from the lower portion of the furnace, and gathers to form accumulations on the side of the furnace near the top of the charge. Such accretions, when not too badly fused by being penetrated by blowholes, are usually comparatively easy to bar off. When the lowerings or fluctuations in temperature cause the volatile material from the bottom part of the furnace to condense in the charge, the charge is made less porous, less gas can penetrate, and the rate of smelting is slower. Then, when the coke at the tuyere burns out, a cavity may be formed. In time, part of the roof burns out, the gas escapes, so the supporting pressure is less and there is also less support for the arch against the side walls of the shaft. When the arch plus the pressure of the gases will no longer support the charge, it drops. On dropping, many new gas channels are formed; the rate at which coke is burned increases as smelting conditions and capacity approach normal. These phenomena are of varying degrees of magnitude and may be regarded as a normal part of lead blast-furnace operations.

It was recommended that a wider area at the tuyere zone probably would allow a larger amount of coke to accumulate, cause more regular blast-furnace operation, and also make it easier to break arches from the sides of the furnace.

SLAGS

Theer are many data on the composition of slags versus their lead content. In general, the metallurgist smelts what he has, and it is often not profitable to add barren diluents to the blast furnace to adjust slag compositions alone. Limestone is one of the few such components added, and this usually is added to the sintering machines partly to increase the porosity of the cake. It has been said that the limits of the richness of the charge to the blast furnace are governed by the richness and consequent fusibility of the charge that it is possible to sinter. (As far as known, no one sinters a charge containing over 56 per cent of lead as PbS, and some men do not like to exceed 43 per cent.) In some plants inert diluents are added to lower the percentage of lead in the sinter cakes. The zinc content of a charge without inert diluents may be large enough to make feasible the volatilization of zinc, and the addition of slag-forming diluents may make the operation unprofitable. The rich lead content of highly zinciferous slag has been one of the chief deterrents to making slag of this type. Table 10 gives the approximate composition of slags.

TABLE 10.—*Approximate Composition of Lead Blast-furnace Slags*

Plant	Percentages								
	Pb	Zn	SiO_2	FeO	S	CaO	MnO	Al_2O_3	MgO
Tooele..........	0.9	5.5	35.4	32.0	1.2	20.2	1.0	Not determined	Not determined
Kellogg.........	1.4	9.6	23.5	33.6	1.6	14.0	3.2	6.6	1.3
Trail...........	4.3	18.0	18.7	37.2	1.4	7.8	1.3	3.7	1.2

PERCENTAGE OF TOTAL LEAD IN SLAG AS

	Metal	Sulphide	Silicate
Tooele....................................	14.7	61.0	24.3
Kellogg....................................	7.2	71.4	21.4
Trail....................................	55.0	17.5	27.5

In general, if the slag becomes richer in lead content at Kellogg the percentage of the lead present as the sulphide increases. At Trail the percentage of metallic lead increases; over 70 per cent of the lead in some dirty slags was present as metal. It is difficult to make a comparison with Tooele because at this plant considerable matte is usually made as a routine matter. With the matte well settled out, the quantity of lead in a slag over the normal content would probably occur mostly in the silicate form.

With the forms of the lead content of slags in mind, reasons can be seen for the relative effectiveness of various methods of decreasing losses of the metal. Thus at Trail, with the lead content of slags already largely in the metallic form, the addition of coke often gives but little assistance.

It is frequently found more effective to add silica than to add coke. Removal of sulphide lead from the slag by the addition of coke is slow and tedious, although coke is an effective reducer for lead in the silicate form.

Some incomplete experiments were performed to determine why the lead in the metallic form at Trail would not settle out of the slag. Spinels, which may be dispersers of metallic lead, were settled out from large amounts of blast-furnace slags kept molten in a small reverberatory furnace. As nearly as could be told from rough measurements and chemical computations, some 9 per cent of the total weight of the blast-furnace slag at Trail occurred as spinels. On the basis of rough estimates, some 7 per cent of the zinc in the slag is in the form of spinels. The spinels contained about 57 per cent of magnetite, 30 per cent of zinc aluminate, and 13 per cent of zinc ferrite. The great bulk of the zinc in the slag very likely occurs as oxide dissolved in fayalite, $2FeO.SiO_2$. In general, when the conditions were more reducing, there was less ferric iron, more sulphur and less lead in the slag. The first of the lead metallized is much purer, except that it is enriched in precious metals and bismuth. At Trail, some of the lead prills taken from slags contained 2.9 per cent of antimony, while the average amount of antimony in the bullion was about 0.8 per cent. It could not be proved, however, that antimonial products dispersed lead. It is well known that lead sulphide will disperse metallic lead through metallic copper, in which otherwise it is quite insoluble. There may be some critical sulphide and other content at which lead is dispersed through slags, but such points were not proved.

Others have found that the time of residence within the furnace affects the lead content of slags. When the volume and distance between the slag tap and the tuyeres were increased at Port Pirie, South Australia, it was possible to lower the lead content from some 2.1 to 1.2 per cent. The time of residence of slag within the furnace at Trail, however, made little difference.

Method of Loading and Capacity of Blast Furnace

Within the usual limits of operation of the lead smelter, the quality of the sinter is the largest single factor governing the capacity. Thus, at Trail over 200 charges (about 300 tons) of charge per blast-furnace day were smelted during a period measured when the furnace had "quality sinter" that was well fused and hard, and would support the weight of the column. Within a considerable range of variation, the constituents of the charge had no notable effect upon the capacity at this time. The slag-forming constituents had the following range: Fe, 28.2 to 30.6; SiO_2, 18.5 to 20.6; Zn, 15.7 to 18.5; CaO, 7.4 to 9.0; Pb. 2.5 to 5.2; and sulphur in the sinter, 1.2 to 2 per cent. Accumulations of sulphides as accretions in the blast furnace lower the capacity of the furnace and by hindering the passage of coke cause lead loss in slags.

The furnaces smelting rich lead charges at Kellogg have long been noted for their great capacity, having made over 200 tons of lead bullion per day and about the same amount of slag. It is true that if lead is present in the sinter in the metallic form it has a low melting point, 327° C., so little time would be required to reduce or melt it. (To reduce lead silicate, it is necessary to increase the quantity of coke and thus to diminish the rate of the smelting so that the slowly reducible lead compounds will descend slowly in thin streams through the incandescent coke.) However, too much metallic lead makes the charge column soggy and difficult to penetrate by the blast, and it would appear that large volumes of metallic lead running over the surface of the coke would obscure its surface and cut down the rate of burning. Such actions would diminish the capacity of the blast furnace; it seems doubtful, then, that the rates of smelting of lead blast furnaces are to be compared on their rates of making slag alone.

It has been noted at several smelters that when the rate of smelting is high the temperature of the slag is comparatively low, whereas the temperature of the bullion issuing from the lead is comparatively high. At Tooele, the average temperature of the slag on tapping is about 1200° C. and of the lead 900°; at Kellogg, 1110° and 950° C., respectively, and at Trail, 1150° and 900° C. When the slag is colder than usual and the bullion hotter, this means that the material was reduced higher up the shaft, that the slag has been somewhat cooled by the incoming air and that the bullion has been longer in contact with the hot slag. Charging the coke so that it formed layers in a Kellogg blast furnace, resulted in less lead in the slag, but the output of the blast furnace was somewhat lower—more of the coke seemingly arrived at the tuyere zone and gave a more reducing atmosphere there.

It has been mentioned that the rate of burning of coke is one of the main factors governing the rate of smelting. At Port Pirie coke of certain porosity burned fastest and gave the fastest rate of smelting. At Trail there was no difference in the rate of smelting when coke "had a porosity" of 42 to 45 and contained 81 to 82 per cent of fixed carbon, and when the coke had a porosity of 50 to 51 and contained 84 to 85 per cent of fixed carbon. (The "porosity" was determined by the Illingworth method.)

It has been noted that rate of flow of air through the tuyeres is very irregular—from 130 to 600 cu. ft. per minute as long as the tuyeres are not completely closed; also that the temperatures vary from a few hundred degrees centigrade to 1400° and over. In keeping with these fluctuations, the composition of the gases at the tuyere zone has varied from that of air to a gas containing over 80 per cent of carbon monoxide. This pointed to the irregular arrival of coke as well as to the irregular arrival of air at the tuyeres. The matter of maintaining the correct balance between the amount of air blown into the furnace and the amount of coke arriving at the tuyeres is then very important.

It is, then, evident that much of the careful work done in preparing a charge of constant composition for the lead blast furnace is likely to be spoiled from the aspect of irregularities in smelting, by the fact there may be large areas within the blast furnace without any coke. It would seem that with more of the charge now composed of sinter less attention is being paid in many plants to methods of charging the blast furnace. It has shown by direct experimentation that if there are no properly placed baffles to guide the falling charge, it may come to rest in such a way that large areas of sinter are left without coke. Charges were actually dropped into blast furnaces and then carefully removed and sampled by hand to determine the correct position of the baffles to distribute the coke better. The proper method of charging, whether the charge is all sinter or not, is determined by the same old fundamental principle that to obtain a uniform rate of flow of the ascending gases, the finer ingredients of the charge should be next to the blast-furnace walls and the coarser toward the center. The precise position of baffle plates by which this result was brought about at the Trail plant is given in *R.I.* 3246. It is to be emphasized that other smelters having different charges and methods of charging should by direct experimental methods determine to what extent the coke is being mixed in uniform amounts in vertical section of the blast furnace and to what extent large vertical areas of charge are being left with but little coke or with an excess of coke.

The important thing is to distribute coke uniformly to each vertical section and to have the ratio between the amount of coke and air supplied at the tuyeres a constant. Since the area of the tuyere opening is that of a punch bar of a given diameter, there is no need for a free opening larger than the diameter of the largest bar that can be conveniently used. From the basis of even distribution of the air and coke, then, it would seem that there should be more tuyeres. This in turn should permit a larger volume of air to enter the furnace, to come into closer contact with the coke, and consequently to smelt more charge. This practice of increasing the number of tuyeres and reducing their size, together with a slightly wider furnace, has resulted in more efficient operation and increased capacity at the Trail plant. These innovations are being incorporated in a new lead blast furnace at Kellogg.

Lead Smelting in the Federal Improved Mechanical Ore Hearth

By L. J. Buck*

Lead smelting in the ore hearth, first practiced in Europe, whence the traditional name "Scotch hearth," and later developed in America to its present efficiency, is based upon the roast reduction process and is applicable to relatively high-grade galena concentrates.

The roast reduction process embraces not only the roast reactions:

$$2PbS + 7O = PbO + PbSO_4 + SO_2$$
$$PbS + 2PbO = 3Pb + SO_2$$
$$PbS + 2PbSO_4 = Pb + 2PbO + 3SO_2$$

but also, by reason of the addition of extraneous fuel, the reduction reaction:

$$2PbO + C = 2Pb + CO_2$$

Thus in the ore hearth the roasting of lead sulphide, forming lead oxide and lead sulphate, the reaction of lead oxide and lead sulphate with lead sulphide producing lead, and the reduction of lead oxide by carbon producing lead, go on simultaneously.

THE ORE HEARTH

Function of the Ore Hearth.—The ore hearth, through the roast reduction process, provides for the extraction of lead and the immediate disposal of the smelting products—fume, hearth slag and lead, all of which are subsequently treated as follows: the fume is recovered in the flue system and baghouses, mixed with concentrates, and returned to the ore hearth in the form of ore mix; the hearth slag is smelted in a blast furnace for the further recovery of lead; and the lead is refined and cast into a marketable product.

Concentrates Amenable to Ore-hearth Smelting.—Only concentrates that are high in lead content, 70 per cent or more, are ordinarily considered amenable to ore-hearth smelting.

Silica should not exceed 2 per cent and iron is allowable only to 4 per cent. These slag-forming constituents occlude both sulphide and metallic lead, prevent the elimination of sulphur and decrease the lead extraction.

Lime and magnesia are beneficial in that both favor a dry slag, promote elimination of sulphur, and prevent occlusions of metallic lead.

Manuscript received at the office of the Institute July 20, 1936.

* Federal Plant. American Smelting and Refining Co., Alton, Ill.

Fluorspar is objectionable, its action being opposite to that of lime, in that it produces a fluid slag. Under certain conditions this constituent, on account of its low fusion point, may prevent treatment in the ore hearth.

Zinc may be successfully treated up to 4 per cent or possibly 5 per cent. This maximum is manifest in the difficulties arising in the subsequent blast-furnace smelting of the resultant hearth slag in which, with the attendant sulphur, the zinc content has been increased approximately fourfold.

Copper may be present up to 2 per cent; however, the formation of matte not only produces a "sticky" condition in the charge but also causes accretions.

Fuel.—Coke breeze, relatively cheap and of high fixed carbon content, is the most suitable fuel, as it fulfills the necessary requirements: low ash, producing a minimum amount of slag; proper size, approximating that of the charge and preventing segregation; and low volatile matter, tending to prevent excessive flue temperatures. When coke breeze is not available or is prohibitive on account of the cost, coal may be used, but precautions must be taken to assure proper baghouse temperatures.

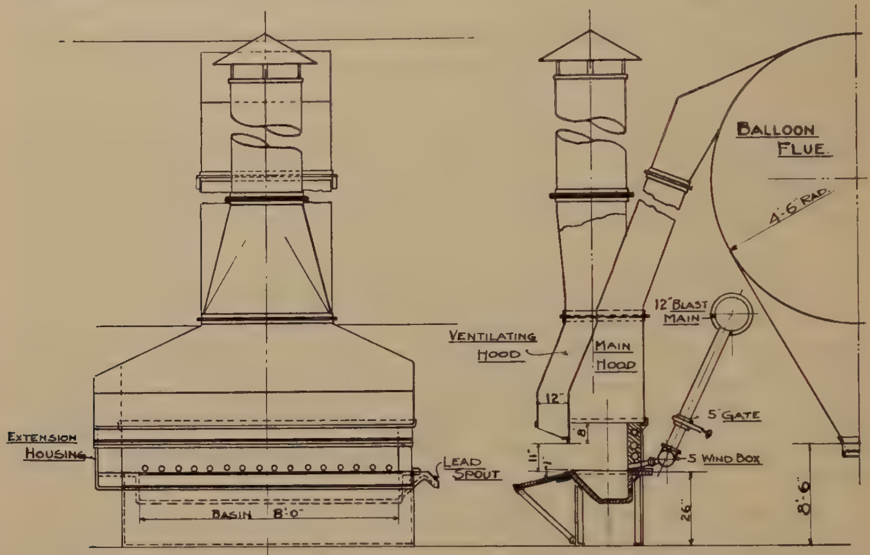
Salient Features of Ore-hearth Smelting.—In a single operation, the ore hearth not only extracts an average of 60 per cent of the lead from the ore mix, which includes the fume returned, or, in terms of new material smelted, yields approximately 80 per cent lead extraction; it also produces a hearth slag, approximately 15 per cent of the ore mix charged, that is low in sulphur and properly agglomerated for blast-furnace smelting.

Although ore-hearth smelting is conducive to a relatively high production of fume, approximately 35 per cent of the ore mix charged, through proper baghouse equipment there obtains a high percentage recovery of the dust, in which the sulphur is practically entirely present in the form of lead sulphate, which, when mixed with the concentrates and returned to the ore hearth in the form of ore mix, hastens the roast reactions to such an extent that the ore hearth handles its own dust burden without loss in the capacity of original materials treated.

THE MODERN ORE HEARTH

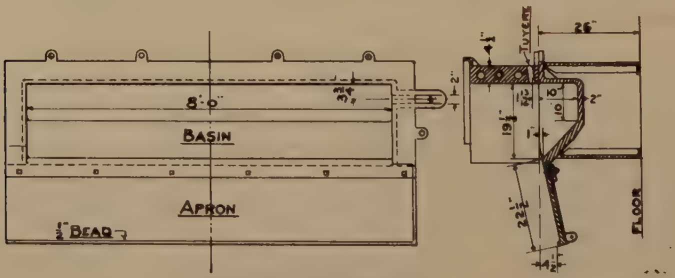
Figs. 1 and 2 show the important details of the basin, apron and jackets, and the general arrangement of the ore hearth with the machine omitted.

The cast-iron basin, average thickness 2 in., is 8 ft. long, 20 in. wide, and 10 in. deep; conveniently supported so that the top is level and 26 in. above the working floor. The back and ends of the basin are vertical, and are flanged at the top. At the right end of the basin, 3¾ in. from the back, there is a 2-in. lead spout. The bottom of the basin is horizontal through 10 in., one-half of the distance from back to front, while the front half slopes up at approximately 45° to the lip of the basin, which is 1 in. below the level of the ends and back. The front of the casting slopes slightly down and forward from the lip forming the back, or start, of the apron. The apron proper, made of 1-in. cast iron, is fastened, by an offset and countersunk bolts, to the front flange of the basin; extends forward 22½ in. from the lip of the basin, with a total down pitch of 4 in., and is beaded along the front.

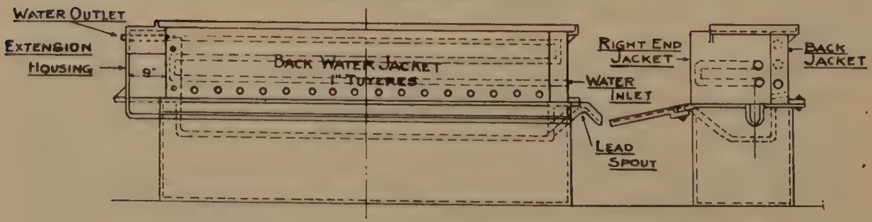


FRONT ELEVATION SECTIONAL ELEVATION

FIG. 1.—GENERAL ARRANGEMENT OF MODERN ORE HEARTH.



PLAN OF BASIN AND APRON



FRONT ELEVATION OF BASIN, APRON AND JACKETS

FIG. 2.—PLAN AND ELEVATIONS, MODERN ORE HEARTH.

A cast-iron water jacket, 18 in. high, 4½ in. thick, and 8 ft. 9 in. long, so as to extend 4½ in. past the inside ends of the basin, is supported by the flanged top of the back of the basin, and forms the back of the hearth. Three 2-in. wrought-iron pipes, with suitable fittings, provide the water space, and are integral with the casting. The back water jacket is cored to accommodate the tuyeres. The right side of the hearth is a similar jacket 18 in. high, which terminates on a line even with the lip of the basin. A 9-in. extension housing, bolted to the back jacket, serves as the left side of the hearth. It is made of 1-in. cast iron, and the bottom conforms to a continuation of the top of the basin and the adjacent 10 in. of the apron.

There are sixteen 1-in. tuyeres, at 6-in. centers, located 1³⁄₁₆ in. above the top of the basin, pitching slightly downward through the back jacket. The tuyere pipes lead from a wind box, made of 5-in. wrought-iron pipe, which has connections at each end to a 12-in. blast main; both connections are provided with 5-in. gate valves.

A steel hood, supported by steel framework, rests on the top of the back and right jackets, and is fastened to the top of the extension housing. The front of the hood extends down 8 in. over the front, or working face, of the hearth, and vertically is 11 in. above the lip of the basin. This, the main hood, is connected to a balloon flue. A ventilating hood is also provided, independently supported by the building proper. The ventilating hood, extending to the left end of the extension housing, is 9 in. longer than the main hood; is parallel to, and set back to front with it; extends down to within 6 in. of the bottom of the main hood; and protrudes 12 in. over the apron.

THE ORE-HEARTH PROCESS

The ore-hearth process itself is perhaps best described without reference to the apparatus by which the furnace is mechanically operated.

The process consists of five steps—charging, rabbling, sorting, shoveling back and tapping lead—each of which is important. They are performed in the order given. A complete cycle requires approximately 4 min. and, aside from a short interval after the charging period, the smelting is continuous; that is, an operating ore hearth is always in blast. The normal blast pressure is 7 oz. Each furnace delivers approximately 1000 cu. ft. of gas per minute; and the temperature of the charge is 1700° to 1800° F. The coke breeze used varies from 10 to 12 per cent of the ore mix charged, and is dependent upon the operators, the nature of the ore mix, and the condition of the fire. To operate an ore hearth by hand requires one or two helpers in addition to the operator, the ultimate results being greatly dependent upon the diligence of the workmen. With the Federal improved mechanical ore hearth to be described later, the skill required has been reduced to a minimum, with only one operator for an ore hearth.

Each ore hearth is provided with an ore car containing the ore mix, a pile of coke breeze, a slag car for receiving the hearth slag, a molding wheel to receive the molten lead, a lead truck, and the proper tools.

With a furnace in blast, the charge is floated on a molten bath of lead and built up by spreading alternately thin layers of ore mix and coke breeze, accompanied by intermittent rabbling and shoveling back, until a normal thickness of charge results, 4 to 5 in. above the lip of the basin.

Assuming that the furnace has been brought in properly, a temperature of 1800° F. obtaining in the charge, molten lead is produced. The molten lead seeps down through the charge and enters the basin, so that the level of the lead bath gradually approaches the lip of the basin. A bar is inserted in the lead spout in order that the lead may be tapped at will.

During the smelting, crusts are formed throughout the charge, which, if not broken up, quickly retard the proper functioning of the operation, in that they prevent the uniform penetration of the blast, cause blowholes and occlude small particles of metallic lead.

Progressing from left to right, the rabbling operation is accomplished with a poker, 1½ in. diameter. The poker, held at right angles to the face of the ore hearth, is thrust downward through the charge at the lip of the basin, to the bottom of the basin, and on to the back; then with downward pressure at the outer end of the poker, the lip of the basin serving as a fulcrum, the inner end of the poker is forced upward through the charge. This action dislodges any accretions tending to form in the basin, breaks up the crusts and mixes the charge, and as the poker breaks through the top of the charge considerable material is thrown out upon the apron, varying in size from small unsmelted particles of the charge to 3-in. balls.

At the working temperature of the charge, the slag-forming constituents fuse, and as they are turned over repeatedly during the rabbling, they coalesce to form a clinker, which in the working gathers material, like a snowball, and assumes a spherical shape. This product is the hearth slag, and is composed of the slag-forming constituents cementing together semismelted particles of the charge; the assay percentage of lead of the conglomerate is approximately one-half that of the ore mix charged.

The hearth slag is recognized by its gray color, and was formerly called "gray slag," perhaps to distinguish it from a bluish black material, of similar shape, known as "sinkers," which is a result of poor working; viz., in a portion of the ore hearth that is not properly worked, crusts of concentrates fuse on the outer side and sink to the level of the lead bath, where, owing to the impulses of the bath caused by the poker, they rise and fall, increasing in size through the cementing of metallic lead and particles of semismelted charge, and either form accretions in the basin or are thrown out upon the apron.

As the particles of various size are thrown upon the apron by the poker, those of greatest size roll farthest forward, whence the first step in the sorting operation. The "gray slag" and the "sinkers" roll to the ½-in. bead at the bottom of the apron, and are readily distinguished; the "sinkers" are broken and returned to the charge; the hearth slag is forked to a slag car.

The small particles of the charge and the slag balls of intermediate size repose on the upper half of the apron. All of this material is shoveled back on to the charge in such a manner as not to disturb the charge at the lip of the basin, but cleaning the apron and delivering a considerable portion of the material against the back of the hearth, and allowing it to roll down to the lip of the basin.

The level of the lead in the basin is maintained slightly below the lip of the basin; this regulates the depth of the charge, insures the penetration of the blast and the proper working of the lead. Tapping is accomplished by removing the bar previously inserted in the lead spout and allowing sufficient lead to flow to individual molds, of which there are 10 in a molding wheel. One mold is filled at a tap and, after cooling, the pigs, weighing approximately 100 lb. each, are removed by hand pick and stacked on a lead truck. Proper temperature of the bath is indicated by a slight color of the lead tapped.

The main hood conducts the fume to a balloon flue, where an average draft of 0.5 in. H_2O is maintained. Natural draft on the ventilating hood clears any fumes arising from material on the apron, and maintains a curtain of air in front of the working face of the ore hearth.

Chronological Development of the Ore Hearth

The early ore hearths had a basin area approximately 2 ft. square and treated hand-sorted galena and jig concentrates with intermittent operation to minimize volatilization, as no effort was made to recover the fume.

Later, the water-jacketed 4-ft. ore hearth was installed, and required two men, one to rabble the charge, and the other to shovel back; the operation became continuous when baghouses came into use.

With the introduction of the Newnam mechanically rabbled ore hearth[1], the length was increased to 8 ft. treating gravity concentrates. However, even the ore hearth equipped with the mechanical poker had its limitations. Two men were required for its operation, the operator tending the rabbling machine and the helper shoveling back. The human element here played a too important part in the operation and sufficient rabbling was seldom accomplished, because few men could follow up, shoveling back, at such frequent intervals. The operator was ever complaining that poor production was due to the helper's end of the work.

---

[1] U. S. Patent No. 1388144.

Finally, with the invention of the Mac Michael mechanical shovel, and its combination with the mechanical poker, establishing the ore hearth as a one-man operation, the ore hearth came into its own by placing the responsibility solely on the operator and providing him with an efficient machine to do the work. This development was accomplished at the Federal Plant of the American Smelting and Refining Co., which owns the Mac Michael patents[2].

FEDERAL IMPROVED MECHANICAL ORE HEARTH

Mounted on a track 1 (Fig. 3), above and parallel to the face of the ore hearth 2, the framework of the machine 3 is suspended from the movable carriage 4. The crankshaft 5, through a series of gears and pinions, is driven by a 1-hp. motor 6; through a clutch 7, sprocket 8 and chain 9, continuous travel from right to left between stops 10 and 11 is imparted to the carriage by bevel gears operating on the right axle 12; through an eccentric 13 and eccentric rod 14, intermittent travel from left to right is imparted to the carriage by a ratchet and pawl 15 operating on the left axle 16. The movements of the carriage and machine through various stops, levers and clutches, may be controlled either automatically

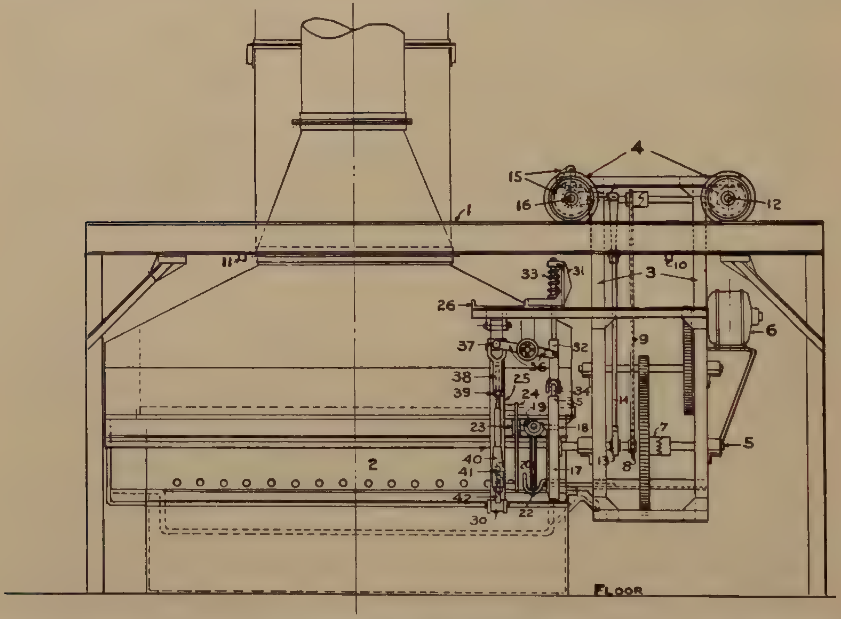


FIG. 3.—FRONT ELEVATION OF ORE HEARTH SHOWING GENERAL ARRANGEMENT, WITH MACHINE AT RIGHT OF ORE HEARTH.
Scale: ¼ inch = 1 foot.

---

[2] U.S. Patent Nos. 1730582, 1733352, 1781025, 1791677, 1791628, 2023483 and 2023484.

or manually; these details and also those providing the adjustments of the moving parts are omitted here in order to avoid undue complication of the small-scale drawings.

Secured to the left end of the crankshaft 5 is the cam wheel 17, Figs. 3–6, to which, by means of a crank pin 18, is attached a U-clamp 19, holding the poker 20. This mechanism causes the poker to execute a movement similar to that described by the dotted line 21 in Fig. 4, the guide 22, attached to the front of the framework, serving as a fulcrum.

Referring particularly to Figs. 3, 5 and 6 for a description of the mechanical shovel, a grooved roller 23, mounted on the left of the U-clamp 19, engages in the guides 24, which are attached to the swing arm 25, pivoted at the top to an extension plate 26 of the framework, and pivoted at the bottom to the shovel arm 27. The forward end of the shovel arm holds the shovel rod 28, attached to the shovel blade 29. The rear end 30 of the shovel arm is forked and pivoted to the lower member of the elevating link. The revolutions of the camwheel effect an up and down movement of the grooved roller between the guides, producing a reciprocating movement of the swing arm, causing the shovel to execute a forward and back stroke.

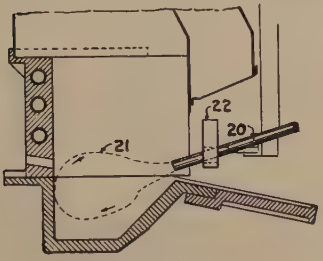


FIG. 4.

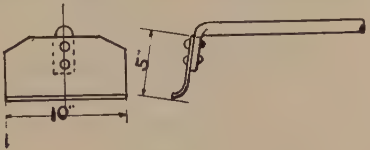


FIG. 5.

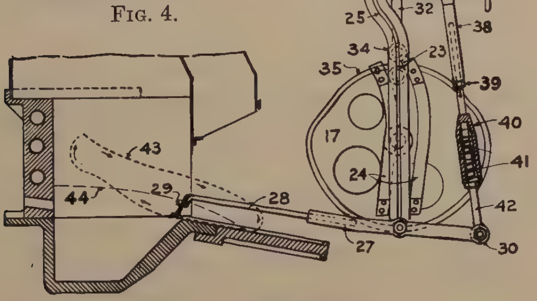


FIG. 6.

FIG. 4.—SECTION SHOWING RELATIVE POSITION OF POKER WITH REGARD TO BASIN, AND MOVEMENT EXECUTED BY POKER.

FIG. 5.—ENLARGED DETAIL OF SHOVEL.

FIG. 6.—SECTION SHOWING RELATIVE POSITION OF SHOVEL WITH REGARD TO BASIN AND APRON, AND MOVEMENT EXECUTED BY SHOVEL.

Scale: ⅜ inch = 1 foot.

A bracket 31, mounted on the extension plate 26 of the framework vertically above the cam wheel 17, supports the follower rod 32, in such a manner that through the tension of the spring 33, the roller 34 is engaged with the cam surface 35. A composite lever 36 connects the follower rod to the universal 37. The upper member 38 of the elevating link is forked to the universal, and through an adjusting nut 39 is connected to the lower member 40 of the elevating link, which is stepped, bored and fitted with springs 41 and piston 42, providing an elastic connection to the forked rear end of the shovel arm. The revolutions of the cam wheel, through its cam surface engaging with the roller, produce an up and down movement of the follower rod, which through a composite lever and universal is transferred to, and so modified by the elastic function of the elevation link as to impart a flip near the end of the forward stroke of the shovel.

The combined mechanisms cause the shovel to execute a movement similar to that described by the dotted line 43 in Fig. 6; the dotted line 44 delineates the surface of the charge immediately following the movement of the poker.

The action of the shovel is important. The first part of the forward stroke, during which the shovel scrapes the apron, is relatively slow; but as the shovel leaves the apron its speed is accelerated until the latter part of the forward stroke is relatively fast, ending in a flip, which throws the material against the water-jacketed back of the ore hearth, and causes it to roll down to the lip of the basin by gravity; producing a selective action by which the finer material is deposited near the top and back, and the coarser material near the bottom and front. A uniform penetration of the blast and an even fire throughout are thus assured. The back stroke is such that the shovel is entirely free from the charge, eliminating packing.

The mechanical shovel is not only a labor saver but accomplishes the work more thoroughly, more uniformly, and at more frequent intervals than can be done manually.

Operation of Federal Improved Mechanical Ore Hearth

Assuming a machine at rest at the left end of an ore hearth in blast, the operator depresses a lever which sets the machine into operation. The machine traverses the front of the ore hearth from left to right, progressing intermittently. Each stage in the progression is composed of two distinct movements; the one, a complete movement of the poker and shovel operating simultaneously, side by side without interference, which pauses as the poker is withdrawn from the charge; the other, during this pause, a movement of the machine approximately 4 in. to the right. During the initial stages, the extension housing permits motion of the shovel while the poker is operating at the left of the hearth, thus avoiding any necessity for a second clutch and associated mechanism for the shovel. The interval of each stage is approximately 2 sec., and the entire traverse, comprising 18 to 20 stages, requires approximately 40 sec.

As the machine reaches the right end of the ore hearth, a stop engages a lever which automatically stops the machine.

The operator next forks the hearth slag into a tip car, pushes the fines to the upper half of the apron, charges ore mix or coke breeze, as the occasion requires, and then pulls a second lever, causing a return of the machine (with the shovel and poker retracted) to the left end of the ore hearth, where it is automatically stopped. The operator then has a rest period of approximately 1½ min. This completes the cycle, which varies from 3 to 4 min. While the machine is traversing the ore hearth lead may be tapped or pig lead may be removed from the molds and stacked on the lead truck.

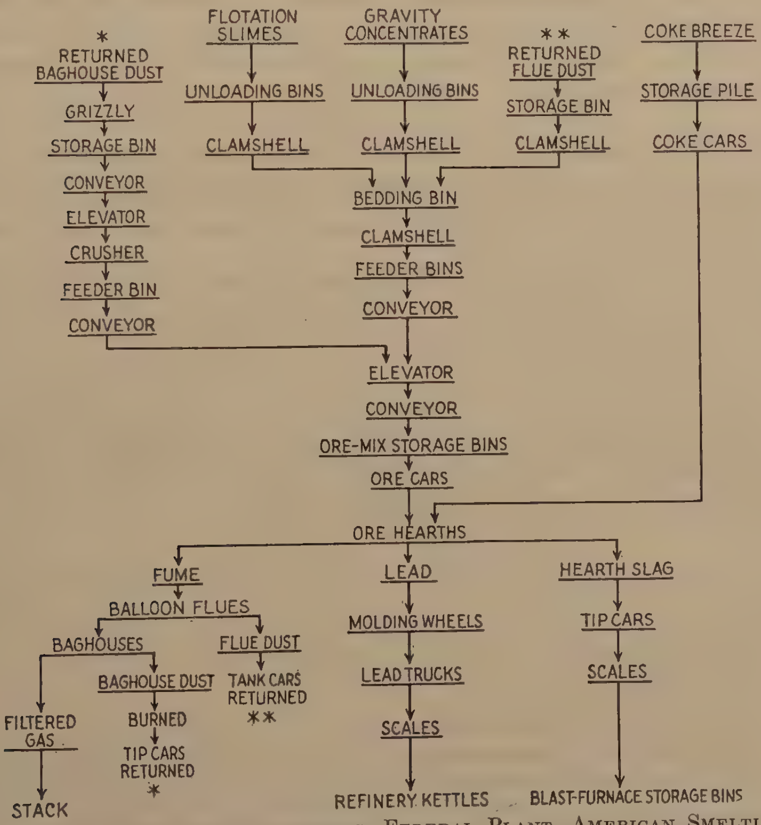


Fig. 7.—Flow sheet of ore hearths, Federal Plant, American Smelting & Refining Co.

The nature of the operation adapts itself to piecework; wages are based upon the number of 100-lb. pigs of lead produced. The ore hearth is operated continuously over the 24 hr.; the men work 8-hr. shifts. The tendency to rob the basin of lead at the end of the shift is countered by the foreman, in cases of dispute, gaging the depth of the lead; if found that the level of the lead in the basin is lower than normal carry, the operator forfeits the required number of pigs to his relief.

A mechanic and an oiler assure the proper adjustments and maintenance of the machines. A motor crew serves the ore hearths with ore mix and coke breeze, delivers the lead and hearth slag to the scales, and thence the lead to the refinery and the hearth slag to the blast-furnace storage bins. The foreman records the weighing of lead and hearth slag.

Pokers of 16 to 18 per cent chromium steel are used, as the longer life well warrants the additional cost. In casting the basins a recess is provided to accommodate filler plates at the lip of the basin, materially increasing the basin's life.

General Arrangement of Federal Ore Hearths

Thirty-one ore hearths are arranged in two parallel batteries, furnaces 1 to 15, and 16 to 31. Each battery, complete with a blower and balloon flue, is housed in a building 75 ft. wide by 425 ft. long. The buildings are 75 ft. apart and staggered. No. 7 furnace of the first battery is opposite No. 16, the first furnace of the second battery, in order to provide a convenient arrangement of both the fuel storage and the mixing plant. An overhead belt conveyor delivers the ore mix to a storage hopper located between the batteries.

Table 1.—*Metallurgical Data*

Constituents	Weight, Per Cent	Analysis, Per Cent					
		Pb	SiO_2	FeO	CaO	Zn	S
Gravity concentrates	47	77.0	0.5	3.5	1.5	2.0	15.5
Flotation slimes	15	72.0	3.0	3.0	2.0	3.5	15.0
Flue dust	8	64.0	2.0	2.5	1.5	1.5	10.0
Baghouse dust	30	67.0				2.0	7.5
Ore mix	100	72.0	1.0	2.5	1.5	2.5	12.5
Hearth slag		38.0	8.0	18.0	6.0	10.0	3.3

Tons total charge smelted per furnace day	18
Tons fuel used per furnace day	2
Tons pig lead produced per furnace day	8
Percentage pig lead extraction	60
Percentage hearth slag produced	15

The ore hearths are spaced at 25-ft. centers with working faces in line, parallel to and in front of the balloon flue and the blast main. Parallel main tracks serve the furnaces at front and back; the front track is provided with a switch and stub track at each furnace for the delivery of ore cars; the back track has two switches and stub tracks at each furnace, the one for spotting a slag car at the left of the ore hearth, the other for spotting a lead truck at the rear of the molding wheel. All equipment is within the building except the blower room which is midway adjacent.

The flow sheet of the plant is shown in Fig. 7.

METALLURGICAL DATA

The figures given in Table 1, although approximate averages, are relative and subject to variations affecting smelting operations.

DISCUSSION

R. L. HALLOWS* AND B. M. O'HARRA,† Galena, Kans. (written discussion).—The construction of the hearths and the method of their operation at the Galena, Kansas, plant of the Eagle-Picher Mining & Smelting Co. are similar to those described by Mr. Buck. At Galena, coal is largely used instead of coke breeze as reduction fuel. The concentrates treated at Galena perhaps average higher in zinc content than those treated at Federal, or at least the zinc content of the flotation concentrates is frequently considerably higher. The chief difference in practice is that whereas the various lead-bearing constituents of the charge are mixed at Federal to give a more or less uniform mixture, at Galena they are delivered separately to the hearths and mixed as charged, the mixture used varying considerably from day to day.

Frequently charges of gravity concentrates only, or of flotation concentrates only, are treated separately, thus making possible a comparison of the metallurgical results obtained from the two types of charge. Flue dust and baghouse dust are usually returned to the charge as produced from day to day. Some flotation concentrates with a lower lead content than is generally considered suitable for ore-hearth treatment are treated; there is not a large enough tonnage of these to warrant the installation of special equipment to treat them by other methods.

The following tabulation gives approximate figures showing comparative metallurgical results when treating 80 and 60 per cent lead concentrates:

	80 Per Cent Pb Concentrate	60 Per Cent Pb Concentrate
Lead in concentrates recovered as metallic lead, per cent....	85	50
Lead in concentrates recovered as lead in gray slag, per cent.	15	50
Dry weight of concentrates as circulating fume, per cent....	24	30
Dry weight of concentrates, coal used, per cent............	4	15
Dry weight of concentrates, limestone used, per cent........	2	12
Concentrates treated per hearth per 24 hr., tons............	28	16
Gray slag produced per hearth per 24 hr., tons..............	8	11
Lead produced per hearth per 24 hr., tons...................	19	4.5

---

[*] Manager, Lead Smelter, Eagle-Picher Mining & Smelting Co.

[†] Metallurgist, Eagle-Picher Mining & Smelting Co.

Equilibrium in Lead Smelting

By S. Frederick Ravitz,* Member A.I.M.E. and Kenneth E. Fisher†

(New York Meeting, February, 1936)

Four liquids are ordinarily present in the lead blast furnace during lead smelting. At the bottom is the lead bullion, which is metallic lead containing about one per cent of impurities, including gold, silver, copper, bismuth, arsenic and antimony. Above this is the speiss, which consists essentially of arsenides and antimonides of iron and copper. The speiss is followed by the matte, which consists principally of sulfides of iron, copper and lead[1]. The top layer is the slag, of which the major constituents are silica, lime, alumina, zinc oxide and iron oxide. Similar products are obtained from the dross furnace, which treats the dross obtained in decopperizing lead bullion.

The distribution of gold and silver among these various products is of considerable importance in the smelting of lead. In general, the matte and speiss cannot be treated in the lead smelter, and usually are sent to a copper smelter. It is usually desirable, therefore, to keep their gold and silver contents as low as possible, and to collect the precious metals in the bullion. If the bullion, speiss, matte and slag exist together in equilibrium, the gold and silver should distribute themselves among these four liquids in a definite manner, which, other conditions being equal, should depend only on the amounts of gold and silver in the charge to the furnace. It is thus apparent that a knowledge of whether such equilibrium exists is necessary before attempting to study the effects of various compositions of matte and speiss on the distribution of gold and silver among the furnace products[2]. Moreover, systems consisting of four liquids in equilibrium are very rare, and are of considerable scientific interest.

In order to ascertain whether equilibrium existed, the distribution of gold and silver among the four liquids was determined. The speiss,

---

Manuscript received at the office of the Institute Nov. 29, 1935.

* Research Metallurgist, Utah Engineering Experiment Station, University of Utah, Salt Lake City, Utah.

† Graduate Assistant, 1934–35, Utah Engineering Experiment Station, University of Utah.

[1] In certain cases either the matte or the speiss may be absent. If the charge to the furnace is very low in sulfur, no matte is formed, while if it is very low in arsenic and antimony, no speiss is formed.

[2] Such a study is now in progress in this laboratory.

matte and slag used in this investigation were dross furnace products obtained from a local lead smelter; granular test lead was used instead of bullion. The analyses of the speiss and matte were as follows:

	Au, Oz. per Ton	Ag, Oz. per Ton	Pb, Per Cent	Zn, Per Cent	Cu, Per Cent	Fe, Per Cent	S, Per Cent	Sb, Per Cent	As, Per Cent
Matte...............	0.16	37.2	15.8	2.9	61.3	1.0	15.8	0.4	2.9
Speiss...............	4.16	88.8	17.4	3.2	58.3	0.6	2.1	2.1	16.1

The composition of the slag was not determined.

Four fusions, each with different amounts of gold or silver, were made in clay crucibles for each experiment. Standard Denver Fire Clay Co. tall-form, size D crucibles, 4 in. high and 2⅜ in. diameter at top, were used, with clay covers. To each crucible was added 50 grams of test lead, of speiss, of matte and of slag (the latter three ground to minus 80 mesh), and the desired amount of gold or silver. The silver was added in the form of powdered silver nitrate, and the gold as gold chloride solution. The contents of each crucible were mixed thoroughly, and the four crucibles were then placed in a large pot furnace and heated to approximately 1250° C. for about ½ hr., after which they were removed and allowed to cool rapidly. The crucibles were then broken away from their contents, which in all cases were found to be in four well defined layers that could easily be separated from one another. Each layer was analyzed for gold or silver, the slag and bullion by ordinary fire assays, and the matte and speiss, because of their high copper contents, by a combination wet and fire method[3].

The results of the experiments are given in Tables 1 and 2. The distribution coefficients K were calculated by assigning the value unity to the concentration of gold or silver in the bullion. These coefficients thus represent the ratios of the concentration of gold or silver in the slag, matte or speiss, as the case may be, to that in the bullion. These tables show that in each experiment the distribution coefficient for gold or silver between bullion and speiss and between bullion and matte (and therefore between speiss and matte) is very constant, regardless of the amount of gold or silver added. For example, although the amount of silver added varies more than threefold, and the amount of gold tenfold, the average deviation of the constant from the mean is less than 2.6 per cent in every case except for the distribution of gold between bullion and matte, in which it is 11.3 per cent. The latter is by no means surprising; because of the small amounts of gold dissolved in the matte, an error of only a few hundredths of an ounce per ton in the assay (the accuracy of which is lowered by the high copper content) would readily account for it. The slight variation of the constants for the three experiments with silver is

---

[3] E. A. Smith: Sampling and Assaying of the Precious Metals, 349. London, 1913. Griffin & Co.

TABLE 1.—*Distribution of Silver in Dross Furnace Products*

$AgNO_3$ Added, Mg	Silver							
	In Bullion		In Speiss		In Matte		In Slag	
	Oz. per Ton	*K*	Oz. per Ton	*K*	Oz. per Ton	*K*	Oz. per Ton	*K*
EXPERIMENT 1								
300	76.4	1.000	94.4	1.236	44.8	0.586	0.24	0.0031
500	99.6	1.000	118.4	1.189	55.6	0.558	0.32	0.0032
700	119.6	1.000	142.0	1.187	66.0	0.552	0.16	0.0013
1000	150.8	1.000	179.2	1.188	83.2	0.552	0.26	0.0017
Mean..................		1.000		1.200		0.562		
Average deviation from mean, per cent..				1.2		2.1		
EXPERIMENT 2								
300	77.2	1.000	94.4	1.223	40.4	0.523	0.16	0.0021
500	100.8	1.000	119.2	1.183	53.2	0.528	0.16	0.0016
700	121.2	1.000	143.2	1.182	63.6	0.525	0.24	0.0020
1000	148.8	1.000	178.4	1.199	78.0	0.524	0.16	0.0011
Mean..................		1.000		1.196		0.525		
Average deviation from mean, per cent..				1.2		0.27		
EXPERIMENT 3								
300	84.0	1.000	92.0	1.095	44.8	0.533	0.8	0.0095
500	110.8	1.000	126.0	1.137	58.8	0.531	1.6	0.014
700	136.0	1.000	162.0	1.191	75.6	0.556	1.2	0.0088
1000	179.2	1.000	204.8	1.143	99.6	0.556	1.2	0.0067
Mean..................		1.000		1.142		0.544		
Average deviation from mean, per cent..				2.2		2.2		

TABLE 2.—*Distribution of Gold in Dross Furnace Products*

$AuCl_3$ Added, Cc.	Gold							
	In Bullion		In Speiss		In Matte		In Slag	
	Oz. per Ton	*K*	Oz. per Ton	*K*	Oz. per Ton	*K*	Oz. per Ton	*K*
1	3.39	1.000	5.3	1.563	0.30	0.0885	0.01	0.0030
3	6.56	1.000	10.9	1.662	0.48	0.0732	0.02	0.0030
5	9.72	1.000	16.6	1.708	0.62	0.0638	0.06	0.0062
10	15.4	1.000	25.8	1.675	1.00	0.0649	0.12	0.0078
Mean..................		1.000		1.652		0.0726		
Average deviation from mean, per cent..				2.6		11.3		

due undoubtedly to slight differences in time or temperature during the experiments. Small amounts of arsenic, antimony or sulfur are probably volatilized during the fusions, and the distribution coefficients are quite sensitive to the composition of the matte or speiss[4].

From a casual inspection of the tables, it would appear that the amounts of gold or silver dissolved in the various layers are not proportional to the amounts added. However, when it is considered that some gold and silver are originally present in the matte and speiss, reasonably good proportionality is found. This is shown in Table 3, which has been calculated from the data in Table 1 for experiment 1. Similar results are obtained for the other experiments.

TABLE 3.—*Relation between Silver Assays and Amounts of Silver Added*

$AgNO_3$ Added, Mg.	Difference	Increase in Silver Assay, Oz. per Ton			Increase in Assay per 100 Mg. $AgNO_3$		
		Bullion	Speiss	Matte	Bullion	Speiss	Matte
300	200	23.2	24.0	10.8	11.6	12.0	5.4
500	200	20.0	23.6	10.4	10.0	11.8	5.2
700	300	31.2	37.2	17.2	10.4	12.4	5.7
1000							
Mean					10.7	12.1	5.4

A further check on the data is afforded by calculating the amounts of silver that would be present in the various layers after fusion if no silver nitrate had been added. Thus from Table 1 it is found that the concentrations of silver in bullion, speiss and matte are in the ratio of 1.000:1.200:0.562 (neglecting the small amount in the slag); i.e., the total amount of silver initially present will be distributed in the three layers in the fractions 1.000/2.762, 1.200/2.762 and 0.562/2.762 respectively. The analyses of the matte and speiss show that if one ton of each of the four products had been used, there would have been 126 oz. of silver present. Multiplying this by each of the above fractions, the concentrations in the bullion, speiss and matte are found to be 45.6, 54.8 and 25.6 oz. per ton respectively.

These concentrations can also be calculated in a different manner. For example, Table 3 shows that in the first experiment the silver concentration of the bullion increases 10.7 oz. per ton for every 100 mg. of silver nitrate added; the silver introduced with 300 mg. of silver nitrate is therefore 32 oz. per ton. Table 1, however, shows that when 300 mg.

---

[4] K. E. Fisher: Distribution of Gold and Silver in Lead Blast-furnace Products. Thesis, University of Utah, 1935.

of silver was added, the concentration was 76.4 oz. per ton. The difference, 44.4 oz. per ton, represents the concentration that would have resulted if no silver nitrate had been added, and agrees well with the value 45.6 found above. The corresponding concentrations for the speiss and matte are 58.0 and 28.6 oz. per ton. Similar results are obtained for the other experiments.

The coefficients obtained for the slag (Tables 1 and 2) are by no means constant, but this is to be expected. Gold and silver are almost completely insoluble in slag, and their presence undoubtedly is due principally to minute inclusions of matte, speiss and bullion, which did not settle out of the slag. Nevertheless, there can be little doubt that the slag is practically in equilibrium with the matte, speiss and bullion. The constituents of these three liquids are almost completely insoluble in the slag, and chemically there is little, if any, tendency for them to react with the slag.

The results of this investigation show that the products of lead smelting—bullion, speiss, matte and slag—exist together in the molten condition in a state of equilibrium. Although the experiments were simple fusions carried out in the laboratory, similar equilibrium conditions unquestionably exist in the blast furnace and the drossing furnace in actual lead smelting.

Acknowledgment

The authors wish to express their appreciation of the late Dr. T. B. Brighton, at whose suggestion this work was undertaken. His ability, encouragement and cheerfulness were a source of inspiration to all his associates.

DISCUSSION

(*Carle R. Hayward presiding*)

C. P. Linville,* Bound Brook, N. J.—This paper seems to go into the fundamental question of equilibrium. My interest has been more in the commercial side of it for a good many years; that is, we had speiss and drosses and things of that sort, and we had to recover gold and silver. That is what we wanted to do. This paper opens up possibilities when thinking of what to do about such a problem. If there is going to be equilibrium, a component that is free from the material that is wanted will take it from the other one until equilibrium occurs. In this particular case, it seems that if lead is added it will become rich in silver and will reduce the amount of silver in the drosses. The same thing would be true to perhaps as great an extent if silver-free matte were added, or if sulphur were mixed with the charge, fused in a reverberatory furnace and matte made without making slag, and got most of the silver in the matte.

On the other hand, I should like to ask whether anybody knows how to get the gold out of speiss.

---

* Metallurgist, The Calco Chemical Co.

S. F. Ravitz.—It happens that we used pure test lead as a substitute for bullion, more or less drawing gold and silver from the matte and speiss into the lead.

C. P. Linville.—We had great quantities of speiss, and by speiss I mean the impure arsenide, leady, coppery speiss containing nickel and cobalt, and we found that we could get the great bulk of the silver out by floating the lead and copper, which we did by brimstone fusion. We mixed the speiss with brimstone and fused on the hearth of a reverberatory furnace, and strange to say over 90 per cent of the brimstone we used was found in the mattes we made, and those mattes carried most of the silver. There would be some left, but the great bulk of the silver was taken out of the residue; although most of the gold remained with the nickel and cobalt and the arsenic and antimony.

S. F. Ravitz.—I think I mentioned that it is comparatively easy to reduce the content of gold and silver by making a high lead-copper ratio in the speiss, but when you do that you are between the devil and the deep blue sea. If you make a high lead-copper ratio, the lead smelter is sending a lot of lead to the copper smelter; on the other hand, if you make a very high copper-lead ratio, the gold in the speiss goes up rather high.

C. P. Linville.—That brings us to the conclusion that it is wrong to ever smelt, if it is possible to avoid it, materials that contain arsenide, particularly arsenide with nickel and cobalt, with any gold-bearing material. They should be kept away from the copper smelter that carries gold, and if possible should be smelted only with lead material. A great deal of low-gold material from the Ontario district was messed up with a great deal of gold in this country, because it got into the copper smelter. If it had been kept with the lead, the amount of gold taken up with that nickel and cobalt would not have been so serious.

F. E. Lathe,* Ottawa, Ont.—From the commercial point of view, the interest lies in the gold and silver content of the slag. I notice that the silver content varied from 0.16 up to 1.6 oz. per ton, and the gold from 0.01 to 0.12 oz. per ton. One would not think of throwing away a slag with that amount of gold. The authors have suggested that the presence of gold and silver in the slag may be accounted for by the inclusion of a certain amount of matte, speiss or bullion. Has any analysis been carried out that would indicate the amount of copper and lead, for instance, in the slag as produced?

S. F. Ravitz.—No, we made no such analysis.

F. E. Lathe.—That would be a very interesting point, and one well worth checking up.

Member.—Why are the experiments made with equal parts of matte, lead, speiss and slag, and why is the silver 1.2 times the assay of the bullion? In a blast furnace there would not be equal parts of slag, lead, and so forth, with, say, 75 per cent lead and the rest made up of speiss, et cetera.

S. F. Ravitz.—The total amount would be different, of course, but the assay of the silver in the speiss, for example, would still be 1.2 times the assay of the bullion, other things being equal.

Member.—What finally becomes of the speiss?

S. F. Ravitz.—It goes to the copper smelter.

---

* National Research Council.

E. L. Jorgensen,* Irvington, N. J.—The authors came to the conclusion that equilibrium exists between silver and gold content of lead bullion, speiss and matte, under the conditions of their experiments. I wish we could talk about equilibrium in the kind of lead smelter I am in charge of. My experience with speiss has fortunately been limited. The lead is used as a collector and travels around and around. Impurities in matte and bullion vary greatly, and with them we have an utter lack of equilibrium. Often the silver content of the matte is as high as in the bullion and occasionally higher. In such cases, the addition of scrap iron will reduce the precious-metal content of the matte and at the same time in the slag.

As to the distribution of precious metals in slags, we have made some observations that may throw a sidelight on the discussion. If we allow a pot of blast-furnace slag to cool so that a crust is formed, break the crust and pour out remaining molten part of the slag, we find that gold and platinum metals are enriched in the crust much more than silver. By utilizing this fact in practice, we have reduced our slag losses as follows: gold, 71 per cent, platinum metals, 61 per cent, silver, 34 per cent.

In practice, the products are not allowed to solidify in contact with one another, and results so obtained are not directly applicable to operating conditions. We know, for instance, that matte in cooling gives off lead, which takes precious metals along.

S. F. Ravitz.—We did some experimenting with the artificial slags, and found some of them had a very much higher gold and silver content. It seems to depend somewhat on the viscosity of the slag, which was one of the things that led us to our conclusion that the gold and silver in the slag are due primarily to inclusions.

Member.—Did you find any difference in the distribution of the silver in the matte dependent on the higher copper content?

S. F. Ravitz.—We made some preliminary experiments in which constant amount of silver were added to mixtures of artificial mattes or speisses of varying composition and test lead. Table 4 shows three of the results obtained in a series of seven experiments with iron-copper-sulphur mattes in which the iron content was successively increased, the copper decreased, and the sulphur held approximately constant. In

Table 4.—*Results of Experiments with Iron-copper-sulphur Mattes*

Experiment No.	Composition of Matte, Per Cent				Silver, Oz. per Ton	
	Iron	Copper	Sulphur	Lead	Bullion	Matte
1	4.9	58.7	20.2	15.2	32.0	13.5
4	32.3	31.6	23.3	13.1	37.3	12.2
7	55.2	6.7	23.9	13.6	38.5	11.5

Table 5.—*Results of Experiments with Iron-copper-arsenic Speisses*

Experiment No.	Composition of Matte, Per Cent				Silver, Oz. per Ton	
	Iron	Copper	Sulphur	Lead	Bullion	Matte
1	4.9	69.1	14.9	11.1	23.3	22.7
4	48.8	28.0	15.9	6.7	38.6	6.3
7	74.6	7.0	14.8	2.7	45.8	1.6

---

* Works Manager, Irvington Smelting & Refining Works.

spite of the great decrease in copper content, the silver in the matte decreased, and in the bullion increased, only slightly. The distribution coefficient for silver in the matte fell from 0.42 to 0.30. Table 5 shows the results of similar experiments with iron-copper-arsenic speisses. The silver in the speiss decreased greatly as the copper decreased, the distribution coefficient dropping from 0.97 to 0.035. An interesting point is that although the solubility of lead in the speiss decreased considerably, its solubility in the matte remained practically constant.

C. A. HEBERLEIN,* Carteret, N. J. (written discussion).—The question was raised as to the best disposal of speiss in smelting operations. I should like to give a concrete example from the lead-smelting operations of the Cia. Minera de Peñoles at Mapimi, Durango, Mexico. From the early nineties smelting operations were conducted at Mapimi exclusively from lead ores mined at the well-known Ojuela mine, about eight miles from Mapimi. Besides lead, silver and gold, the ore had a rather high arsenic content, producing during smelting operations a large quantity of speiss. Despite the most strenuous efforts, speiss used to accumulate and tie up considerable quantities of lead, silver and gold.

Through the acquisition of the Torreon smelter and the gradual exhaustion of the Ojuela mine, the difficulties in handling speiss lessened, but during the peak days of smelting operations at Mapimi, from the year 1900 to 1918, the question of handling the speiss in such a way as to prevent it from re-entering direct smelting operations was of the most serious concern, both metallurgically and commercially. After many attempts the problem was solved in the following manner: The smaller blast furnaces were replaced by large ones, in order to assure a free flow of lead from the Ahrents siphon. After several years of experimentation with different forehearths, the conclusion was reached that the best and cleanest work could be done through the use of an oil-fired separator or settling reverberatory placed at one end of the furnace building. Speiss, matte and slag together were intermittently tapped from the blast furnace into a covered slag ladle and, by means of an overhead crane, carried to and poured into the separator. Using covered slag ladles, a very small amount of shells was produced; in fact, small enough to permit the resmelting of large amounts of old slag dumps carrying considerable values in lead and silver.

In the separator considerable lead bullion settled out and was tapped into bars. Speiss and matte were tapped to produce thin slabs to be crushed into a convenient size and roasted to complete elimination of the arsenic. Adhering strictly to the foregoing system, the accumulation of speiss was definitely prevented. The arsenic was expelled into the air, but the lead, silver and gold returned to the smelting circuit.

The slag overflowed from the separator into slag pots and disposed in the usual manner over the dump. After the introduction of the oil-fired separator the whole process of disposing speiss and matte was simplified to such an extent that the tie-up of lead, silver and gold was reduced to a minimum and accumulation of speiss prevented. The wet lead in the slag varied from 0.8 to 1.0 per cent with a very low silver content. In order to reduce the difficulty of crushing the speiss, it must be well settled and free from metallic lead, an object that was rather easily accomplished in the separator.

H. R. HANLEY,† Rolla, Mo. (written discussion).—The theme of this paper is the equilibrium of distribution of gold and silver among the products formed in smelting; viz., lead bullion, speiss and matte. Under the laboratory conditions, the authors obtained a reasonably constant ratio of concentration of gold and silver in the bullion, speiss and matte. The authors are now studying the effect of various compositions of matte and speiss.

---

* Director of Research, U. S. Metals Refining Co.

† Professor of Metallurgy, Missouri School of Mines.

It is known that variations in the content of speiss and of matte will cause variations in the solubility of gold and silver therein. Hofman* says: "As regards the presence of precious metals the fact is to be noted that speiss retains considerable amounts of gold, whereas very little gold is found in the matte. Speiss assays show from trace to 0.5 oz. gold per ton. The presence of metallic iron in speiss furnishes an explanation for the excess of gold over silver usually found, as iron has a strong affinity for gold."

There will be a variation in the metallic iron and copper in speiss and matte depending upon the chemical and mechanical factors operative in the blast furnace. Consequently, the same equilibrium condition as noted in the laboratory tests could not be assumed to exist in practice, as the authors imply. Furthermore, the formation of speiss, matte and slag in commercial blast-furnace smelting proceeds differently from that of crucible smelting. In the blast furnace, the eutectic mixtures of products are formed first and flow away first, leaving the more refractory products to follow.

The melting of preformed products in a crucible yields final products more homogeneous, or less heterogeneous, than it is possible to attain in the blast furnace. Consequently, the two types of furnace operations—blast-furnace ore smelting and crucible fusion of preformed products—are not comparable. It is highly probable, however, that in the melting of matte, speiss and bullion in a *drossing furnace*, conditions approximating those of the crucible would exist. The relative solubility of the precious metals in these three products, in this case, would be governed by the composition of speiss and matte.

S. F. Ravitz.—We meant by no means to imply that the *same* equilibrium conditions exist in practice as in our laboratory tests. In fact, we attributed the slight variation in our distribution coefficients to differences in composition of the mattes and speisses resulting from small differences in time or temperature during the experiments, and we specifically mentioned that "the distribution coefficients are quite sensitive to the composition of the matte or speiss" (p. 121). This is well shown by the data given on page 124.

As Mr. Hanley says, the formation of slag, speiss, matte and bullion within the blast furnace represents conditions far removed from equilibrium. In considering equilibrium among these products, however, the processes by which they are formed are, from a thermodynamic point of view, immaterial. Although eutectic mixtures may be formed first, they will soon meet, as they descend the shaft, products melted from the lower and more refractory parts of the charge, and by the time the crucible of the furnace is reached, all the products will ordinarily be molten and well intermixed (this is particularly true with the prevailing use of charges consisting mostly of sinter, coke being about the only constituent of the charge that gets into the crucible in the solid state). Indeed, it is not unlikely that they will already be fairly close to equilibrium.

Within the crucible the four liquids exist in definite layers, although there is a continual "rain" of the heavier liquids through the lighter. This condition is particularly favorable for the attainment of equilibrium. How closely true equilibrium is approached depends upon a number of factors. Among these are: (1) nearness to equilibrium of the products when they reach the crucible; (2) length of time in the crucible; (3) constancy and uniformity of temperature; etc.

It appears probable that the products, to a large extent, are preformed when they reach the crucible of the blast furnace, and that conditions within the crucible do not differ greatly from those in a drossing furnace or even in a small laboratory crucible. Perhaps the most important difference is that newly formed products are continually being added to the crucible of the furnace.

---

* Metallurgy of Lead, 386. New York, 1918. McGraw-Hill Book Co.

Drosses in Lead Smelters

By C. M. Dice,* Junior Member A.I.M.E., G. L. Oldright,† Member, and T. B. Brighton‡

(New York Meeting, February, 1934)

The base bullion from the lead blast furnace contains varying amounts of the impurities left in the smelter feed by the concentrator, regardless of the method of smelter operation. These impurities may be held in part in mechanical suspension rather than being present as true alloys. However, usually there is little free space in the crucible in which to separate these drosses before the bullion is taken from the lead well.

When such a dross is melted in a laboratory crucible and allowed to cool, the products obtained are lead bullion, speiss, and matte in well separated layers. Typical analyses of layers are:

Element	Analyses, Per Cent		
	Bullion	Speiss	Matte
Pb	92.0	41.2	38.3
Cu	2.4	36.3	40.6
As	4.0	16.5	4.3
Sb	0.7	0.2	0.4
S	0.6	1.9	13.1
Fe	0.0	0.0	0.0
Totals	99.7	96.1	96.7

The absence of iron in these products drossed from the blast-furnace bullion proves that the impurities for the greater part are not simply finely divided blast-furnace speiss or matte that has been dissolved or dispersed in the lead, but are held in solution by the liquid metal and rise to its surface as infusible compounds when the temperature of the bath is lowered. In general, the drosses made locally are metal sulphides and arsenides and not oxidized compounds. The large content of metallic lead also does not seem to be retained because of oxidized compounds

---

This paper presents the results of work done under a cooperative agreement between the United States Bureau of Mines and the University of Utah. Published by permission of the Director, U. S. Bureau of Mines. Manuscript received at the office of the Institute Dec. 1, 1933; revision received Sept. 14, 1936.

* Former Research Assistant, Utah Engineering Experiment Station, University of Utah, Salt Lake City, Utah.

† Supervising Engineer, Lead and Zinc Section, Metallurgical Division, U. S. Bureau of Mines, Salt Lake City, Utah.

‡ Late Research Metallurgist, Utah Engineering Experiment Station, University of Utah, and member A.I.M.E.

that form films around particles of metallic lead and thereby "stabilize an emulsion." The amount of metallic lead in drosses was not decreased by the addition of coal to a drossing reverberatory at a temperature of 2600° F.

OBJECTIVES OF PARTIAL SOFTENING

The main problem in the partial softening operation at lead-smelting plants is to increase the copper and decrease the lead content of the matte or speiss produced from dross and later sent to the copper plant. The objectives of conducting this step at the western lead smelters are: (1) to increase the capacity of the refinery making a finished product, (2) to remove copper nearer to a copper smelter adapted to handling it, (3) to save more of the metallic lead skimmed off in drosses, and (4) to save freight on the impurities removed.

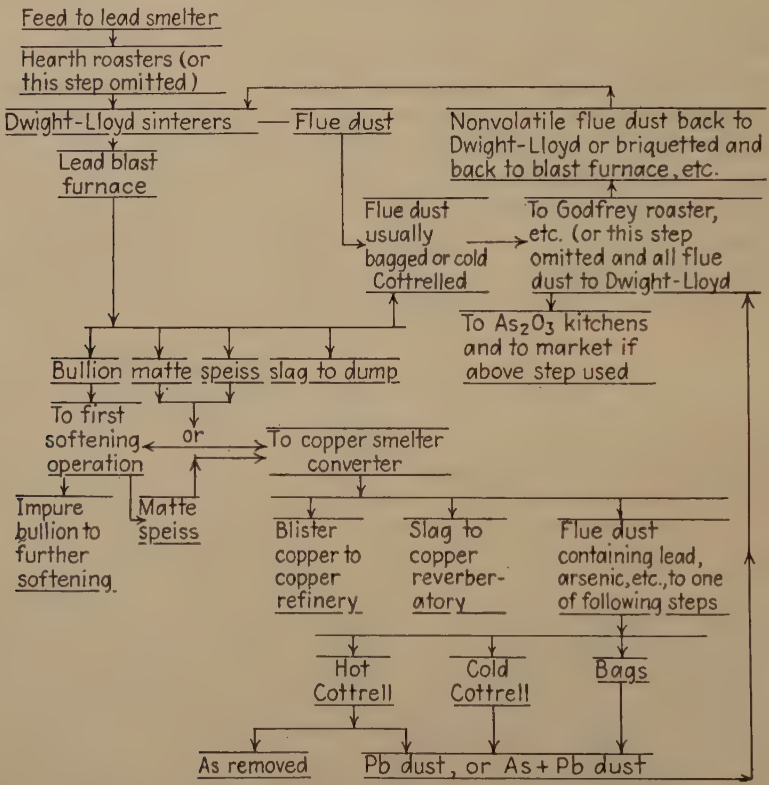

Feed to lead smelter
Hearth roasters (or this step omitted)
Dwight-Lloyd sinterers
Flue dust
Nonvolatile flue dust back to Dwight-Lloyd or briquetted and back to blast furnace, etc.
Lead blast furnace
Flue dust usually bagged or cold Cottrelled
To Godfrey roaster, etc. (or this step omitted and all flue dust to Dwight-Lloyd
To As_2O_3 kitchens and to market if above step used
Bullion
matte
speiss
slag to dump
To first softening operation
or
To copper smelter converter
Impure bullion to further softening
Matte speiss
Blister copper to copper refinery
Slag to copper reverberatory
Flue dust containing lead, arsenic, etc., to one of following steps
Hot Cottrell
Cold Cottrell
Bags
As removed
Pb dust, or As + Pb dust

FIG. 1.—FLOWSHEET OF COMBINED LEAD AND COPPER SMELTER.

The operations of the lead and copper smelter for the removal of impurities, particularly those that are volatilizable, are, then interlocked, as shown on the flowsheet in Fig. 1.

As great an amount of sulphur is removed on the sintering machines as is compatible with the production of hard, strong, sinter cakes. Only smelters making considerable amounts of copper matte need some sulphur. The removal of arsenic and antimony as volatile oxides from roasters or blast furnaces depends upon the surface of these minerals exposed and the extent to which they are present in the "ous" condition. The pentavalent forms of arsenic and antimony are much more slowly volatile than are the more reduced forms. For these reasons, arsenic and antimony may be volatilized more readily from hearth roasters than from blast roasters such as the Dwight-Lloyd. Much less of the antimony than of the arsenic is volatilized, as the latter has a higher vapor pressure. The higher oxides of arsenic and antimony may be reduced to lower forms by sulphur-bearing and carbon-bearing compounds. In operating the blast furnace, the addition of either scrap iron or coke takes arsenic out of the bullion. If the quantity of lime in the charge is reduced so that the silica has to combine with iron the arsenic is forced to enter the matte or bullion. When the matte is rich in copper the amount of arsenic in the bullion is small. (In U. S. Patent 1803771, R. C. Rutherford roasts off the sulphur so that an excess of copper is present to combine with arsenic.)

In general, a volatilized product, such as arsenic or lead, may be removed from the dust caught in the Cottrells or baghouses of the copper and lead smelters. Thus, in the lead plants the Godfrey roaster treating flue dust may be operated at such a temperature that the arsenic will volatilize and be segregated in separate kitchens. In the copper plant it is possible to separate the volatilized arsenic and antimony from the lead by running hot the first Cottrells treating converter gases, and thus first stopping the lead. When arsenic is too abundant on the market and both the copper and lead plants wish to have the other carry the entire burden of removing arsenic from their combined circuits, an enormous circulating load is built up on both plants.

Treatment of Mattes and Drosses in Lead Smelters

Formerly, the general practice was to roast the first matte and add it as iron flux to the blast-furnace charge. The resultant second matte, after roasting, was smelted with blast-furnace slag either in a lead or copper furnace. After two or three successive smeltings the enriched matte was sent to the copper works. The commonest practice today is to treat the matte in a small reverberatory furnace or to send the unconcentrated matte to the converter. A flowsheet (Fig. 2) is shown for plant B. At plant A the flowsheet is somewhat similar, except that the drossed bullion is cast and sent direct to the refinery. By using the drossing reverberatory the costs of concentrating by roasting and resmelting are largely avoided, and the variations of operation inherent in the irregular arrival of impurities in the bullion are largely smoothed out. One plant sending matte from the lead blast furnace to the converters has found that the copper content ranges from 10 to 30 per cent, lead from 10 to 15, arsenic around 15, and sulphur around 20, while the amount of iron present is both large and variable, to make up the remainder of the matte. Typical analyses of the matte and speiss from the blast furnace of another local plant are as follows:

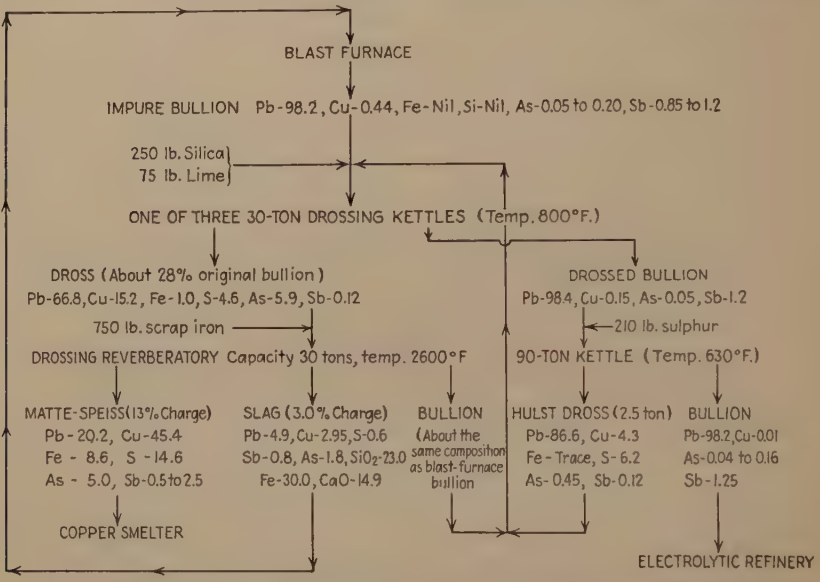

BLAST FURNACE
IMPURE BULLION Pb-98.2, Cu-0.44, Fe-Nil, Si-Nil, As-0.05 to 0.20, Sb-0.85 to 1.2
250 lb. Silica
75 lb. Lime
ONE OF THREE 30-TON DROSSING KETTLES (Temp. 800°F.)
DROSS (About 28% original bullion)
Pb-66.8, Cu-15.2, Fe-1.0, S-4.6, As-5.9, Sb-0.12
750 lb. scrap iron
DROSSING REVERBERATORY Capacity 30 tons, temp. 2600°F
MATTE-SPEISS (13% Charge)
Pb-20.2, Cu-45.4
Fe - 8.6, S - 14.6
As - 5.0, Sb-0.5 to 2.5
COPPER SMELTER
SLAG (3.0% Charge)
Pb-4.9, Cu-2.95, S-0.6
Sb-0.8, As-1.8, SiO2-23.0
Fe-30.0, CaO-14.9
BULLION
(About the same composition as blast-furnace bullion
DROSSED BULLION
Pb-98.4, Cu-0.15, As-0.05, Sb-1.2
210 lb. sulphur
90-TON KETTLE (Temp. 630°F.)
HULST DROSS (2.5 ton)
Pb-86.6, Cu-4.3
Fe-Trace, S-6.2
As-0.45, Sb-0.12
BULLION
Pb-98.2, Cu-0.01
As-0.04 to 0.16
Sb-1.25
ELECTROLYTIC REFINERY

Fig. 2.—Incomplete flowsheet of softening operation, plant B.

Product	Analyses, Per Cent								
	Cu	Pb	Fe	As	Sb	S	Zn	CaO	SiO$_2$
Matte	5.9	9.5	48.8	1.5		20.0	5.4		0.7
Speiss (low As)	6.0		50.5	17.8	8.0	7.2	0.6	0.3	1.6
Speiss (high As)	2.9	1.4	60.8	28.8		3.8	0.2		0.2

In comparison, the following products are removed fairly consistently from the drossing reverberatory at the composition shown, the analyses being from two plants making different products:

Product	Analyses, Per Cent						
	Pb	Cu	As	Sb	S	Fe	Total
Speiss	15.4	48.1	14.8	6.4	4.0	6.0	94.7
Matte	20.2	45.4	5.0	0.5	14.6	8.6	94.3

Drossing Practice

After the dross has been charged into the reverberatory it is heated for about 2 hr. at 2400° to 2600° F., and slag is tapped. Scrap iron in amounts up to 2 per cent may then be added, and the same temperature held for 4 to 5 hr. longer. The fusion becomes quiet after about 2 hr. but is maintained for another 2 or 3 hr. to give pellets of lead an opportunity to settle out. Lead is then tapped to the appearance of matte. Then the matte is tapped from the opposite side of the furnace and granulated by a strong jet of water. The granulated matte is loaded into cars and sent to the copper smelter for converting.

In the endeavor to remove more of the lead, modified flowsheets have been tried, thus (1) no scrap iron has been added or (2) matte and speiss have been tapped separately. The addition of scrap iron up to 2 per cent lowered the amount of lead in the final matte-speiss between 3 and 5 per cent, seemingly by replacing part of the lead combined with sulphur. No more benefit was derived by the addition of more iron. It was thought at another plant that the addition of iron freed enough copper from Cu_2S to form Cu_3As, which retained less metallic lead than the Cu_2S.

A comparison of the following analyses of the mattes and speisses produced on settling the two separately and together showed that the amounts of lead contained in the two sets of products were about the same. The method of tapping speiss into pots was then abandoned, and the combined matte-speiss product is being granulated as before.

Product	Analyses, Per Cent				
	Cu	Pb	Fe	S	As
Matte (granulated)	56.4	23.2	1.2	14.4	2.9
Speiss (settled)	54.0	19.2	0.2	5.4	12.2

The function of the sulphur in the Hulst process is supposedly to combine with the copper to form Cu_2S. As will be pointed out later, this reaction occurs to a certain extent. However, it has been found that the addition of nearly any fine material, including finely ground limestone, garden earth, etc., will cause copper to form a scum on top of the bath. The addition of such material seems to collect the finely dispersed copper and to act as a flocculator, as in flotation. It was found, however, that the copper content of the bullion could be lowered most by the addition of sulphur. Putting sulphur into the kettle dross does not seem to increase the lead content of the reverberatory matte, but it does lower the amount of arsenic from about 8 to 4.5 per cent: as noted, heating with sulphides causes more arsenic to volatilize.

In general, it may be said that for a plant using a dross reverberatory the amount of arsenic volatilized and the composition of the other products made (final matte and amount of lead separated) will vary with the amount of sulphides, copper arsenic and scrap iron added. The function of other ingredients added, as lime and siliceous ore, is chiefly to aid in charging the reverberatory.

EXPERIMENTAL WORK

Composition of Lead Dross, Matte and Speiss

The products chosen for this study were from a plant treating a comparatively simple ore, to avoid the large variations in the kinds of impurities in more complex ores. The analyses of the various types of matte, speiss and dross produced are given in Table 1.

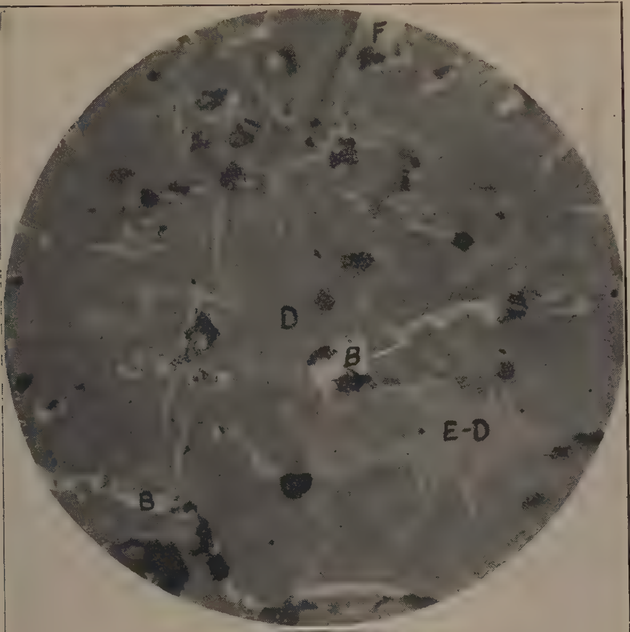
TABLE 1.—*Analysis of Matte, Speiss and Dross*

Product	Product from	Analyses, Per Cent							Total Determined	Photomicrograph
		Pb	Cu	As	S	Sb	Fe	Pb (Metallic)		
Matte I.....	Dross reverb., start tap	20.0	44.7	2.7	16.9	0.19	10.4	10.4	94.89	Fig. 3
Speiss I.....	Dross reverb., start tap	20.2	43.8	19.2	3.1	1.16	10.0	14.6	97.46	Fig. 4
Matte II....	Dross reverb., end tap	19.4	44.6	2.3	17.0	0.43	10.9	10.4	94.63	
Speiss II....	Dross reverb., end tap	20.2	44.1	14.9	6.0	0.81	8.3	16.0	94.31	
Matte III...	Dross reverb., settled	22.3	52.0	2.9	13.5		1.0		91.7	Fig. 5
Speiss III...	Dross reverb., settled	26.7	47.5	12.0	3.3		1.3		90.8	Fig. 6
Matte IV...	Dross reverb., settled	23.0	55.2	2.9	12.4		0.6		94.1	
Speiss IV....	Dross reverb., settled	18.7	53.3	15.0	3.4		0.4		90.8	
Dross B.....	Lead well	82.3	1.5	1.1	3.5	0.06	4.2	57.2	92.66	
Dross I.....	Kettle No. 1	65.6	16.7	7.6	3.5	0.25	0.2	41.9	93.85	
Dross II[a]....	Feed reverb.[a]	66.8	15.2	5.8	4.6	0.12	1.0	40.2	93.52	
Dross H.....	Hulst	86.6	4.3	0.5	6.2	0.12	Tr.	60.1	97.72	

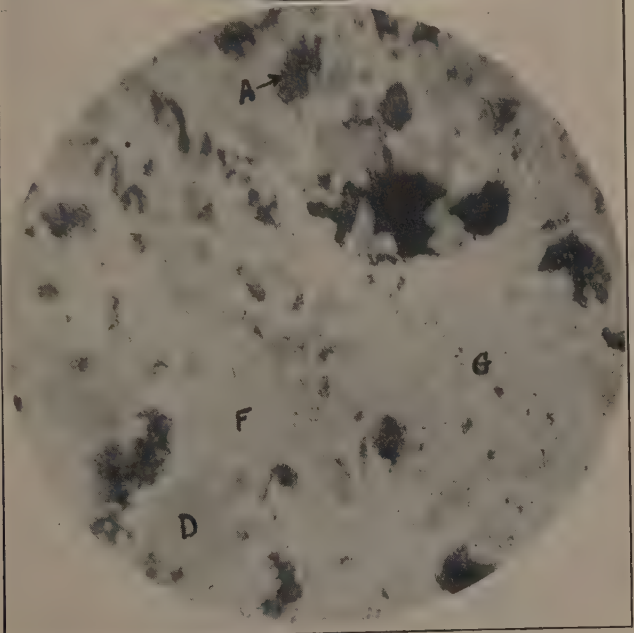
[a] Dross I mixed with Hulst dross.

The samples of dross as taken contained a considerable amount of siliceous ore in rather large pieces, and these as well as the large pieces of dross were screened off. Only the minus 10-mesh material (which had about the same composition as the composite sample) was used for the study. It was found by sieve analyses that the majority of the sulphides and arsenides concentrated in the finest sizes; for instance, one minus 200-mesh product contained some 10 per cent of arsenic compared with 3.4 for the minus 10-plus 14-mesh material. Although there is a trend in the expected direction, the difference does not seem large enough to separate various ingredients by sieving the untreated dross. Methods employed in concentrating ores suggest themselves for separating the various ingredients, but only pyrometallurgical methods were tried.

The dross samples were prepared for microscopic examination by fusing at a temperature of about 1250° C., and cooling slowly to allow the lead to settle as much as possible. The cooled samples were then sawed in half; one half was polished and the other reserved for chemical analysis.



3



4

Fig. 3.—Section of matte 1. × 200.

Showing primary CuFeS crystals *D* plus the eutectic *E-D*. Areas *B* are seams of metallic copper. The metallic lead, *A*, usually occurs with the included speiss crystals *F*. (Tables 1 and 3.)

Fig. 4.—Structure of speiss. × 200.

Copper arsenide, *F*; $x\text{Cu}_2\text{S}.y\text{FeS}$, *D*; metallic lead, *A*; and probably iron arsenide, *G*. (Tables 1 and 3.)

The drosses had separated into two and sometimes three well defined layers. Dross I contained a top layer that was mainly sulphides; a middle layer of a mixture of sulphides and arsenides, and much metallic lead; and a bottom layer consisting mainly of metallic lead. Dross II separated into the same kinds of layers, except that there was a smaller quantity of the middle layer. The Hulst dross comprised a top layer of sulphides, a center layer of metallic lead containing a considerable quantity of sulphide material, and a bottom layer of metallic lead. Fig. 7 illustrates the separation of dross I into these layers. The section of the

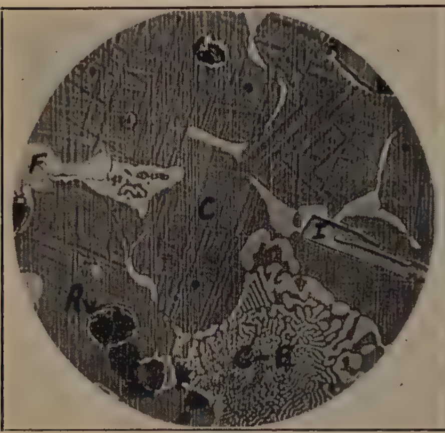


Fig. 5.

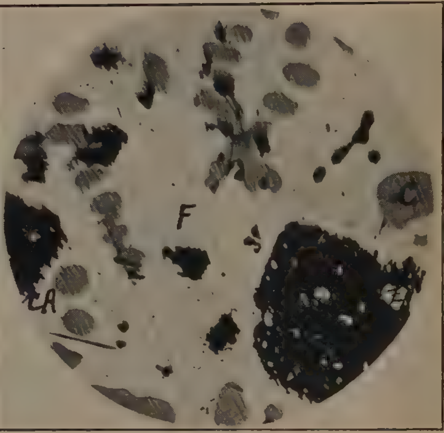


Fig. 6.

Fig. 5.—Section of matte III. × 200.

Showing Cu_2S(*C*), Cu_2S-PbS eutectic (*C-E*), metallic lead, *A*, speiss, *F*, and an unknown crystal *I*.

Fig. 6.—Section of speiss III. × 200.

Showing Cu_2S(*C*); metallic lead, *A*; copper arsenide, *F*, and probably a higher copper arsenide, Z.

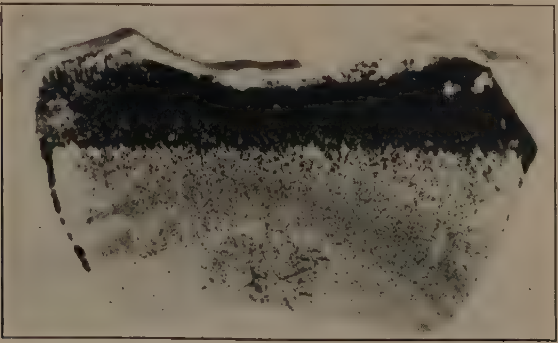


Fig. 7.—Polished section of dross I. × 1.5.

Showing separation into matte, speiss and lead layers.

photomicrograph, Fig. 8, is taken across the junction of the matte-speiss layers.

The various dross samples were further separated along the dividing meniscus of the layers, which were analyzed separately, as shown in Table 2.

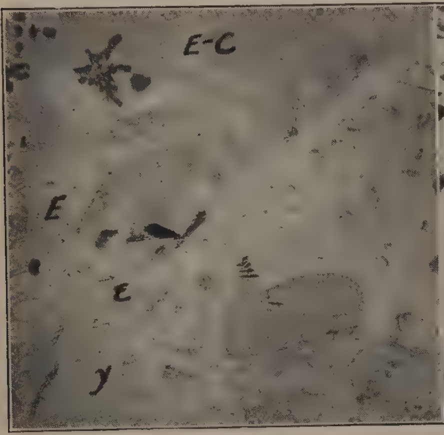


Fig. 8.

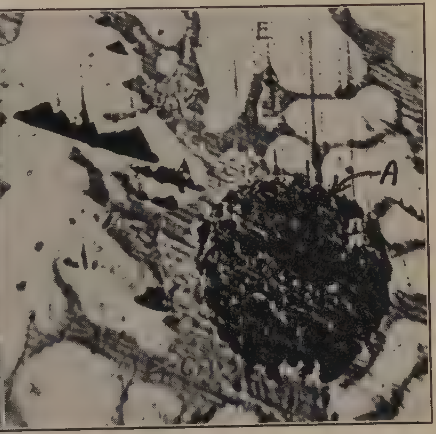


Fig. 9.

Fig. 8.—Meniscus dividing matte and speiss layers of dross, Fig. 7. × 200.
Matte shows primary crystals of PbS (*E*) in PbS-Cu_2S eutectic (*E-C*). Dark areas are metallic lead. Speiss area shows copper arsenide partly transformed to *E* and also some matte that has not separated completely. (Table 3.)

Fig. 9.—Structure of sulphide layer of Hulst dross. × 200.
Light primary crystals are lead sulphide, *E*. Cu_2S occurs with PbS as eutectic *E-C*. The large crystal *A* is metallic lead. (Table 3.)

Table 2.—*Drosses Separated into Layers by Slowly Cooling Fused Melts*

Dross from	Layer	Analyses, Per Cent					
		Pb	Cu	As	Sb	S	Fe
B—lead well	Top	39.1	2.8	0.9	0.3	13.0	13.7
	Bottom	90.4	1.7	1.3	0.5	0.6	Tr.
I—kettle	Top	38.4	40.5	4.3	0.4	12.1	Tr.
	Middle	51.2	28.6	13.9	0.2	1.7	
	Bottom	84.2	5.1	4.6	0.7	0.6	
II—kettle	Top	44.6	35.7	3.4	0.4	11.7	0.4
	Middle	78.0	8.9	7.8	0.4	1.0	
	Bottom	84.0	6.0	5.4	0.3	1.6	
H—Hulst	Top	72.4	12.3	0.4	0.1	12.5	Tr.
	Middle	91.5	4.2	0.6	0.3	3.7	
	Bottom	96.1	0.8	0.6	0.1	1.0	

COMPOUNDS PRESENT IN MATTE, SPEISS AND DROSS

Methods of Identification

The compounds could be more definitely identified by comparing the unknown crystals under the microscope with synthetic fusions of a known composition. Differences in color and hardness were relied upon nearly always. Various etch reagents applied by Short[1]* as to natural copper, lead, and iron sulphides and arsenides were used. By employing these methods the following compounds have been identified as occurring in the mattes, speisses, and drosses described. The artificial compounds were difficult to distinguish from the reactions of the etch reagents, so the following descriptions may be of service:

Metallic Lead.—This material is easily recognized; it does not take a polish and thus always appears rough and dark under reflected light. The extreme softness of this material is also an aid to its identification. Some of the metallic lead is found in the matte areas but the majority is closely associated with the arsenical material.

In the "middle section" of drosses I and II (Table 2) the lead takes a fair polish, presents a much smoother appearance and is light brown. This same appearance of the lead was noted in some of the synthetic copper-lead-arsenic fusions and is no doubt due to the presence of arsenic. An accurate estimate of the amount of arsenic present cannot be made, but it is known that small smounts of arsenic harden lead appreciably, also that lead and arsenic are miscible in nearly all proportions in the liquid state.

Metallic Copper.—Under reflected light this material shows a copper color and answers all tests for metallic copper. It occurs most frequently as long, thin seams or as small crystals within or adjoining the Cu_2S-FeS crystals. This is probably the so-called "moss copper" discussed by Tiedemann and others.

Cuprous Sulphide.—Under reflected light this material is gray-blue. The crystals usually present a rather smooth, uniform surface, and this compound is the softest one present.

Cuprous Ferrous Sulphide.—Under reflected light this material varies from a gray-blue to purplish blue, depending upon the quantity of FeS contained. As pointed out by Carpenter and Hayward[11], Cu_2S may hold up to 50 per cent of FeS in solid solution. By comparing the smelter products with artificial fusion of FeS, it was found that FeS does not exist as individual crystals in the mattes or drosses under consideration. Crystals of this substance are light brown and present a rather rough, pitted surface. From consideration of the Cu_2S-FeS ratio of the mattes, it has been determined that these crystals are Cu_2S holding about 30 per cent of its weight of FeS in solid solution. The presence of FeS does not seem to destroy the identity of the Cu_2S, which has the same eutectic structure with PbS, regardless of the presence of FeS.

---

* References are at the end of the paper.

Lead Sulphides.—Under reflected light this material shows the characteristic whiteness of galena. The triangular pits that develop in polishing also serve as a means of identification. This substance shows a slightly higher relief than the cuprous sulphide. In all samples in which both cuprous sulphide and lead sulphide occurred together a eutectic of the two was formed, which was rather fine in texture and of typical structure.

Copper Arsenides.—Under reflected light these crystals are various tones of white. The lavender modification of the compound Cu_5As_2 has been found in some of the dross sections. The arsenide present in the matte sections is probably Cu_5As_2 with some Cu_3As_2 in solid solution, as the crystals are dull white compared to the pure compound Cu_5As_2. These crystals were identified by comparison with artificial fused copper arsenides, and their exact composition is doubtful. The substance is slightly harder than any of the sulphides.

Iron Arsenides (Fe_2As).—This crystal has not been positively identified in the drosses. Under reflected light it is a light cream and has a slightly greater hardness than the copper arsenides. These crystals occur in long, narrow areas in the speiss section and may be a double arsenide of copper and iron.

Included Slag.—Under reflected light these crystals appear dark brown. They are very small, present a smooth surface, and occur only near the top of matte sections, indicating a comparatively low specific gravity. This substance has only been found in the matte.

Copper Antimonide (?).—In one of the later samples of matte containing practically no iron (matte III) still another kind of crystal was found. Under reflected light this crystal appears pink and is soft. No effort has been made to identify this crystal positively; however, the antimony content of the matte (2.5 per cent) might suggest that it is a copper antimonide.

Correlation of Chemical and Microscopic Analyses

The calculated percentage of each compound present in the various dross, matte and speiss products is given in Table 3. These calculations are not thought to give the exact percentages of all the compounds just listed as identified under the microscope, but afford some idea of the distribution of the major elements determined chemically. For example, chemical analyses indicated that the dross samples contained practically no iron, and microscopic examination showed no metallic copper. Therefore, the values given for the dross samples were obtained by calculating all arsenic to Cu_5As_2 (which will be within 2 to 3 per cent of the actual

TABLE 3.—*Calculated Amount of Each Compound in Dross, Matte and Speiss*

1 Material	Chemical Analysis, Per Cent							9 Calculated Per Cent Metallic Pb	10 Percentage Metallic Cu Estimated under Microscope	Calculated Amounts of Compounds, Per Cent								19 Photomicrographs
	2 Cu	3 Pb	4 S	5 As	6 Sb	7 Fe	8 Total			11 PbS	12 Cu_2S[a]	13[b] CuFeS	14 Cu_5As_2[c]	15[d] Fe_xAs_y	16 As[e]	17 Sb[e]	18 Total	
Dross I: Top	40.6	38.3	13.1	4.3	0.4		96.7	4.8		38.6	39.4		13.4			0.4	96.6	Fig. 8
Middle	36.3	41.2	1.9	16.5	0.2		96.1	36.3		5.6	5.7		46.8		1.5	0.2	96.1	Fig. 8
Bottom	2.4	92.0	0.6	4.0	0.7		99.7	90.4		1.8	1.8		1.2		3.7	0.7	99.6	
Dross II: Top	35.7	44.5	12.3	3.0	0.4	0.4	95.9	12.8		36.6	36.7		9.4			0.4	95.9	
Middle	21.6	60.8	1.7	12.1	0.4		96.6	56.4		5.1	5.1		25.4		4.5	0.4	96.9	
Bottom	3.0	89.3	0.4	5.2	0.2		98.1	88.3		1.2	1.1		3.1		4.3	0.2	98.2	
Dross H: Top	12.0	72.9	12.7	0.3	0.1		98.0	9.3		73.4	14.2		0.9			0.1	97.8	Fig. 9
Middle	3.2	90.1	3.7	0.7	0.3		98.0	70.0		23.2	2.4		2.0			0.3	97.9	
Bottom	0.6	95.4	0.5	0.5	0.1		97.1	92.3		3.6			0.9		0.2	0.1	97.1	
Matte I	44.7	20.0	16.9	2.7	0.2	10.4	94.9	8.8	2.0	12.9		61.9	9.0			0.2	94.8	Fig. 3
Speiss I	43.8	20.2	3.1	19.2	1.1	10.0	97.4	20.2				12.8	51.9	11.5		1.1	97.5	Fig. 4
Matte II	44.6	19.4	17.0	2.3	0.4	10.9	94.6	13.8	2.0	6.5		66.2	7.7			0.4	94.6	
Speiss II	44.0	20.2	6.0	14.9	0.8	8.3	94.2	20.2				24.5	42.3	6.4		0.8	94.2	

[a] Probably contains traces of FeS.

[b] Calculated percentage of solid solution of FeS in Cu_2S. The ratios Cu_2S:FeS were as follows: for matte and speiss I, 2.8; for matte and speiss II, 2.87.

[c] Copper arsenide present in dross sections is probably Cu_5As_2 with, sometimes, excess arsenic in solid solution, while that of matte and speiss is probably a solution of Cu_3As and Cu_5As_2. For the drosses, then, the arsenide was calculated to Cu_5As_2 and for the matte and speiss the arsenide was calculated to Cu_3As plus Cu_5As_2 in the ratio of 1:1.

[d] Under the microscope Fe_2As was tentatively identified. The arsenide as calculated here contains about 30 per cent As.

[e] Probably occurring with the metallic lead or in solution with some of the other crystals.

arsenide present), the remaining copper to Cu_2S, the remaining sulphur to PbS, and the remaining lead to metallic lead. Where enough copper was not present to form Cu_5As_2 with the arsenic, the remaining arsenic was considered to be present with the lead in the eutectic percentage, as determined by Heike[2], or approximately 3.1 per cent As.

The microscopic study of the mattes, speisses and drosses from smelters showed that the compounds found in these products that exert the greatest influence on the amount of lead retained in the matte-speiss products occur in the copper-lead-sulphur, copper-lead-arsenic and copper-lead-iron-sulphur systems. Examples have already been given to show in general that drosses on being remelted and recooled divided into three layers that are mainly sulphides, arsenides and bullion. From an experimental study of the individual systems involved one then should predict accurately their behavior in a single melt.

Phase Systems Involved in Formation of Matte-speiss Products

It is probable that many of the sulphide and arsenide systems with two base metals should each be considered as ternary rather than binary because of the difficulty of determining the composition of the end members. For the purpose of comparison the systems will be considered both as binary and ternary wherever the data are available.

Lead-copper-sulphur System

Fig. 10 shows that the Pb-Cu-S system may be further divided into several binary systems. The Cu-Pb system is described by Friedrich[3]. A diagram is given by Hofman[4]. Lead and copper are mutually insoluble in the solid state. In the liquid state the solubility curve cuts the liquidus at 953° C., the points of intersection corresponding to 15 and 65 per cent Cu. The upper point on the solubility curve is at 1025° C. The PbS-Pb system has been investigated by Friedrich and Leroux[5], who show a curve dropping from the melting point of the sulphide to that of lead, with no eutectic point, and practical insolubility of the constituents in each other in the solid state. The present work shows a region of immiscibility which extends from 4.9 to 9.7 per cent S at freezing temperatures.

The Cu_2S-Cu system behaves much the same as the Fe-S system. Here the eutectic lies at 96.2 per cent Cu and freezes at 1067° C. Copper and Cu_2S are practically insoluble in each other in the solid state. It has been found that Cu_2S is the only compound of copper and sulphur existing in the fused state[6].

The Cu_2S-PbS system as discussed by Fulton and Goodner[7] is binary. The diagram shows a eutectic at a composition of about 51 per cent Cu_2S with a freezing point of 540° C. The two branches of the liquidus drop in flat curves from the fusion points of PbS and Cu_2S (1114° and 1121° C.), respectively, to the eutectic point. The series is eutectiferous throughout, implying but little reciprocal solubility of constituents in the solid state. These results agree very well with those of Meisner, who considered the system as ternary (Fig. 10). The triangular diagram is divided into three smaller triangles by the lines Pb-Cu_2S and PbS-Cu_2S. In the first triangle, Cu-Pb-Cu_2S, only three kinds of crystals exist. In the binary system, Cu-Pb, there is shown a region of partial miscibility in the liquid state from 35 to 85 per cent Pb; with the system Pb-PbS a similar region exists from 5 to 10 per cent S. Within this triangle there is a region of partial miscibility in which theoretically three liquid layers should occur. Actually, there is an emulsion of the two lower layers due to the presence of sulphur. In the second triangle Pb-Cu_2S-PbS there is a region of partial miscibility which falls very near the line PbS-Cu_2S. Without the addition of lead there is no region of partial miscibility, but only a eutectic mixture. In the last triangle PbS-Cu_2S-S the mixtures cannot be prepared without decomposition.

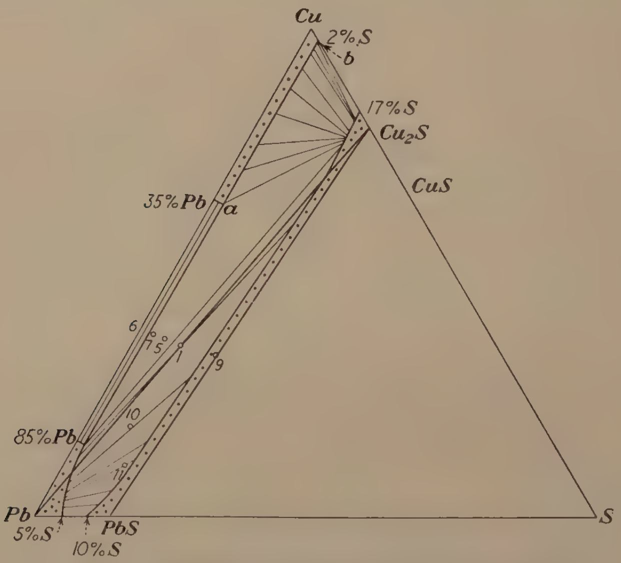


FIG. 10.—LEAD-COPPER-SULPHUR SYSTEM. (*After Meisner.*)

The metallic copper that occurs in the matte samples is usually within or along the boundaries of the Cu_2S-FeS crystals. In some samples, however, it was found adjoining areas of PbS-Cu_2S eutectic (Fig. 3). Theoretically, copper should replace lead in galena, according to the reaction: $PbS + 2Cu = Cu_2S + Pb$. Some further experimental study of the copper-lead-sulphur system was therefore desirable to determine: (1) whether the above reaction proceeds quantitatively, and (2) the amount of metallic lead retained in copper-lead mixtures containing varying amounts of sulphur.

For this purpose pure galena was mixed with pure copper, fused in porcelain crucibles, and allowed to remain at a temperature of about 1300° C. for 2 hr. in the proportions shown in Table 4. With one exception these fusions, which all lie on the line PbS-Cu (Fig. 11) proved to be divided into two layers with a rather sharp line of demarcation. In fusion No. 1 the small amount of metallic lead that had formed occurred as small drops distributed throughout the section. The quantity of the lower layer, which consisted mostly of metallic lead, of course, increased with the amount of metallic copper added. The results of this series of fusions are given in Table 4 and summarized in Fig. 11.

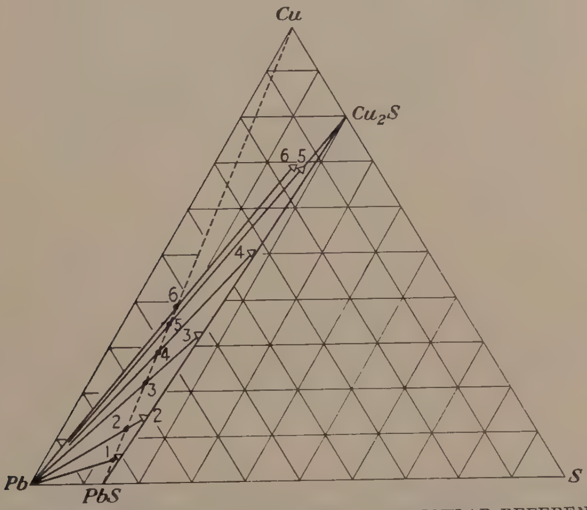


FIG. 11.—LEAD-COPPER-SULPHUR DIAGRAM, WITH PARTICULAR REFERENCE TO SYSTEM LEAD-COPPER SULPHIDE-LEAD SULPHIDE.

Under the microscope, the upper layers of fusions 1, 2 and 3 show primarily crystals of PbS in a eutectic of PbS and Cu_2S together with small amounts of metallic lead. Fusion 4 shows primary crystals of Cu_2S in the eutectic, and also small drops of metallic lead. Here we are on the Cu_2S side of the eutectic point, which, according to Meisner, lies at about 51 per cent Cu_2S. Fusion 5 shows only Cu_2S containing small amounts of lead and fusion 6 the same, together with a small amount of metallic copper.

The position of point 5 on the line Pb-Cu_2S (Fig. 11) clears up the first point in question; namely, that the reaction for the replacement of lead in galena by copper must be a quantitative one as written. If this were not true, some copper would be present in the fusion, which would place the point within the part triangle Pb-Cu-Cu_2S. Although the microscope showed a very small amount of metallic copper in the lead layer, this may be accounted for by considering the loss of sulphur in fusing. The coexistence of metallic copper and lead sulphide in the sections of mattes from smelters, then, is due either to insufficient contact of the two within the furnace, which is highly improbable, or to a modifying effect of some other ingredient. Iron sulphide, which reacts with copper-sulphur mixtures at comparatively low temperatures to give the so-called moss copper, is probably the main modifier[12]. (Compare Fig. 3, of material containing iron and metallic copper, with Fig. 5, of material having no iron and no metallic copper.) That this separation of metallic copper is due to the presence of iron is further evidenced by

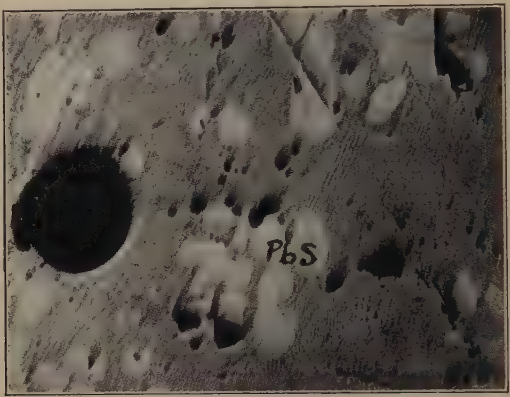


Fig. 12.—Section of fusion 3. × 200.
Primary PbS in PbS-Cu_2S eutectic. (Table 4.)

Table 4.—*Upper Layers of Cooled Fusions in the System Lead-copper-sulphur*

Fusion	Layer	Analyses, Per Cent				Original Mixtures Melted, Grams		Copper Used[a]
		Cu	Pb	S	Metallic Pb, Calculated	PbS	Cu	
1		5.5	81.2	13.2	4.9	40	2.13	10.0
2	Top	14.0	72.5	13.5	1.4	40	5.31	24.9
2	Bottom	2.8	95.4	1.8				
3	Top	31.4	51.9	15.2	3.3	40	10.64	50.0[b]
3	Bottom	0.8	98.5	0.7				
4	Top	49.7	34.0	16.2	9.4	40	15.93	74.8
4	Bottom	0.6	97.9	0.5				
5	Top	67.0	13.2	15.8	14.9	40	21.28	100.0
5	Bottom	5.7	92.8	1.5				
6	Top	68.4	12.8	15.1		40	23.38	100.7
6	Bottom	10.3	87.3	0.6				

[a] Per cent of stoichiometric for the equation $PbS + 2Cu = Cu_2S + Pb$.
[b] Fig. 12.

the fact that matte-speiss samples that do not contain iron do not show metallic copper. This is true even when the copper content of the iron-free mattes reaches 55 per cent.

The amount of lead retained by Cu-Pb-S mixtures has been determined by Meisner, whose results are summarized in Table 5, and Fig. 10. He found only small amounts of metallic lead retained by PbS-Cu_2-S mixtures. As a check on this work the composition of the upper layers of the fusions of Table 4 were placed in the diagram (Fig. 11) and are indicated by triangular points. The first five all lie within, or on, the boundary lines of the part triangle PbS-Cu_2S-Pb. This shows that all the copper present in the upper layer of fusions 1 to 5 is probably combined as Cu_2S. On this basis the amounts of metallic lead present in the upper layers were calculated and are included in one of the columns of Table 4. The quantity of metallic lead retained evidently corresponds to the solubility of the lead at the temperature of solidification, which was probably about 1100° C. It is to be expected, therefore, that the amount of lead retained by either pure Cu_2S or pure PbS will be greater than that retained by mixtures of the two, since the temperature of solidification of the eutectic lies at about 540° C. The following summarizes the calculations made:

	Calculated Per Cent		
Fusion	Cu_2S	PbS	Metallic Pb
1	7.0	88.1	4.9
2	17.5	81.1	1.4
3	39.8	56.9	3.3
4	62.2	28.4	9.4
5	85.1	0.0	14.9

Fusion 1 probably does not represent a true equilibrium because enough lead to form two layers was not present.

It is reasonable to expect that the amount of metallic lead retained by these fusions would be considerably influenced by: (1) temperature of fusion, (2) time the fusion is allowed to remain in the molten state, and (3) quenching. To determine the effect of these factors, four series of fusions were made, the results being summarized in the following paragraphs. The samples were heated in a muffle at temperatures from 1000° to 1300° C. for periods of ½ to 3 hr. and then cooled at various rates. Since we are here concerned primarily with Cu_2S-PbS mixtures, all of the following fusions were made to come within the part triangle PbS-Cu_2S-Pb. The amount of metallic lead was calculated, starting with the assumption that all copper is combined as Cu_2S, as was done above.

The temperature of fusion of PbS-Cu_2S-Pb mixtures seems to have little relationship to the amount of metallic lead retained by the cooled sulphide layer. Less lead was retained by the mixtures that were held fused more than 2 hr., particularly mixtures containing some 60 per cent and more of Cu_2S, or mixtures that approached pure PbS. The fastest

TABLE 5.—*Lead Retained by Copper-lead-sulphur Mixtures*
ACCORDING TO MEISNER

Point[a]	Composition of Material before Melting, Per Cent				Loss on Melting, Per Cent	Thermal Effects	Number of Layers	Layer 1	Layer 2	Layer 3
	Cu	Cu_2S	S	Pb						
1[b]	34.71		8.76	56.54	(*a*) Considerable (*b*) 0.5	925[c] 327 1026 329	3 2	Cu_2S with emulsion of little drops of lead. Very little lead as texture on grain boundary.	Primary segregations of Cu_2S and copper in one basic mass of lead.	Copper.
2 3 4		70 80 90		30 20 10	1.4 4.0 1.8	1030 951[c] 327	3 2 2			Copper.
5	36.9		4.38	58.72	0.4	1032 946 327	2	Cu_2S with little lead and traces of copper.	Emulsion of Cu and Pb.	
6	38.45		1.25	60.3	0.0	952 327	1		The same lead liquated strongly downward.	
7	38.09		2.0	59.91	0.0	942 327	2	Cu_2S quantity of layer is small.		
8	48.5	48.5		3.0	0.0	1102 1052 944	2	Cu_2S with some copper and lead.	Cu with some Cu_2S. Almost free from lead.	
9	31.91		16.1	51.99	1.0	648 535	1	Primary PbS in eutectic of Cu_2S-PbS.		
10	21.0		10.59	68.41	1.0	637 543 327	2	Primary PbS in eutectic of Cu_2S-PbS.	Fairly pure basic mass of lead without any noteworthy primary segregations.	
11	10.5		89.5		1.0	927 540 315	2	Primary PbS in eutectic of Cu_2S-PbS.		
12	CuS 35.0		PbS 65.0		Very considerable	558 516 452	1	Primary PbS in eutectic of Cu_2S-PbS and also a yellow and dark lavender or purplish crystal.		
13	60.0		40.0		(*a*) Very considerable (*b*) Very considerable	564 537 484 Not very good	1			

[a] For position of main points see Fig. 10.
[b] 2 Cu:S:Pb::34.71:8.76:56.54; total 100 per cent.
[c] Brought about by copper as a consequence of a loss of sulphur.

rate of cooling was to drop the temperature from 1300° to 1000° C. in 30 min. When the melts were cooled at slower rates within the limits of the experiments there was but little lessening in content of metallic lead.

For many samples equilibrium is reached after a period of about 2 hr. in the molten state, irrespective of the temperature employed. Once equilibrium has been established, the solubility of lead in the mixtures is evidently that obtaining at the freezing temperature of the melt. The results would indicate that this equilibrium is reached rapidly enough so that the temperature at which the melt is made exerts little influence on the amount of metallic lead retained.

Although the diagrams show that lead is soluble in pure PbS to the extent of 20 to 25 per cent and in pure Cu_2S about 15 to 20 per cent, these substances cannot be held responsible for the reaction of much of the metallic lead in the smelter mattes since, as shown, the matte consists of the mixtures of the two sulphides that contain only minor quantities of lead.

Copper-iron-lead-sulphur System

The investigation of the Cu-Fe-Pb-S system also was started by the use of a number of pseudobinary diagrams.

FeS is shown by Fulton and Goodner to be a chemical compound and the lowest artificial iron sulphide. The eutectic between Fe and FeS has a composition of 16 per cent Fe and 84 per cent FeS and freezes at 970° C. The components of this eutectic are solid solutions of FeS. (Leitgebel[8] states that sulphur is not held by iron in solid solution.) Sulphur is not appreciably volatile from FeS at temperatures below 1500° C.

The system PbS-FeS was investigated by Weidmann[9] and the related system PbS-Fe_7S_8 by Friedrich[10] with practically the same results. These investigators show a eutectic composition of about 26 per cent FeS, with a freezing point at 782° C. The two branches of the liquids drop in almost straight lines to the eutectic point from the fusion ts of PbS and FeS. The system is eutectiferous throughout, implying but little reciprocal solubility in the solid state. In the more recent ternary system Pb-Fe-S by Leitgebel last quoted (Fig. 13) the triangles represent the composition of the upper layer resulting from cooling fused mattes of original composition represented by the correspondingly numbered dots. From the diagram it can be seen that metallic lead is soluble in liquid FeS

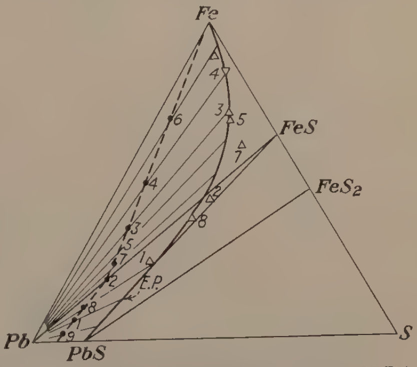


FIG. 13.—LEAD-IRON-SULPHUR SYSTEM. (*After Leitgebel.*)

to the extent of about 30 per cent (point 2). Thus from the curve it would appear difficult to free all of the lead from a copper-lead matte containing much iron sulphide. An increase in the amount of metallic iron beyond point 3 separates no more lead, owing to the corresponding amount of FeS formed. The eutectic composition (E.P.) between FeS and PbS given here is approximately the same as that noted above.

The equilibrium diagram for Cu_2S-FeS as determined by Carpenter and Hayward[11] is produced in Fig. 14. The system forms a solid solution at the FeS end of the series with limiting solubility at about 92.5 per cent FeS and at the Cu_2S end of the series with the limiting solubility at 50 per cent Cu_2S. The eutectic range in the solid state extends from about 92.5 to 50 per cent FeS. A transformation in the solid state at high temperature between the same limits is also present. The eutectic composition lies at about 68 per cent FeS and has a melting point of 995° C. There are no indications of the presence of chemical compounds and no evidences of transformations in the solid state at low temperatures.

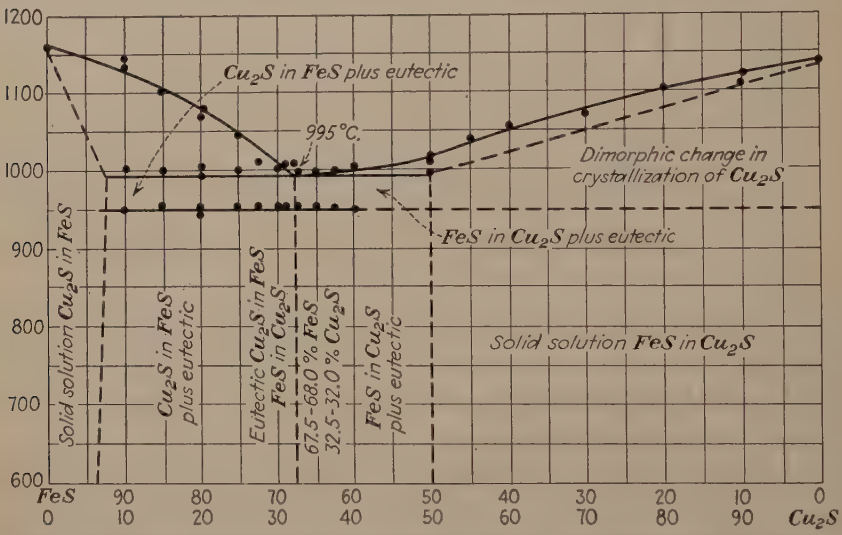


FIG. 14.—COPPER SULPHIDE-IRON SULPHIDE SYSTEM. (*Carpenter and Hayward.*)

Tiedmann[12] and Reuleaux[13] have studied the copper-iron-sulphur system and its relation to copper-iron mattes. Tiedemann's results explained the possible presence of various copper-iron-sulphur compounds which have been reported found in copper mattes, and also the formation of moss copper. Fig. 15 shows the position in the ternary diagram of the various copper-iron-sulphur minerals. With one exception all these minerals occur on the line connecting Cu_2S and Fe_2S_3. The closed line of the figure shows the area in which moss copper was observed. According to these investigators the maximum separation of moss copper occurs between 60 and 62 per cent Cu. Above 71 per cent and below 6 per cent Cu, it completely disappears. Fig. 15 gives the boundaries of the types of crystals found in copper mattes. In section *a* only the pure Cu_2S was found. In part *b*, a structure designated by Reuleaux as "decomposition structure" was observed, being a mixture of $2Cu_2S.FeS$ that had changed to $(Cu_2S)5Fe_2S_3$ and metallic copper. Since the percentage of iron in copper-lead mattes seldom exceeds 10, the other sections have little application to the present work, but are of great interest mineralogically. Section *c* contains bornite and metallic copper; section *d* shows the three kinds of crystals, chalcopyrite, bornite and ferrous sulphides; section *e* contains chalcopyrite and ferrous sulphide; and section *f* contains only ferrous sulphide.

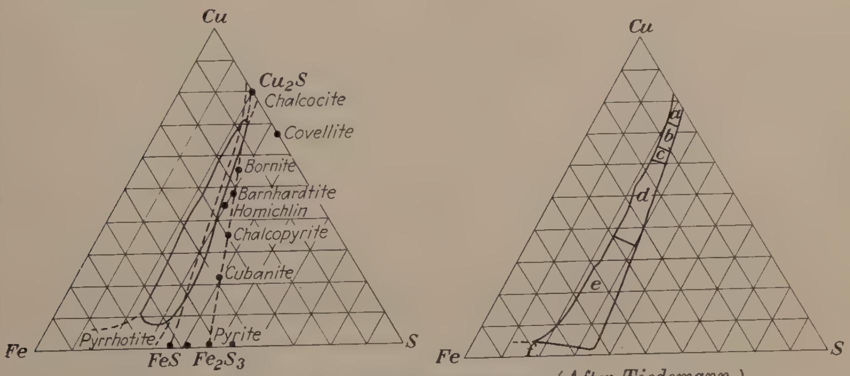


FIG. 15.—IRON-COPPER-SULPHUR SYSTEM. (*After Tiedemann.*)
Area *b* region of moss copper.

It has been shown that a considerable amount of lead sulphide exists in some mattes. Excluding any possible effects of the other constituents of the matte, the addition of iron should replace the lead in lead sulphide and thus lower the final lead content. As a mixture of FeS and Cu_2S fuses at a lower temperature than pure Cu_2S, the mixtures would contain less lead at their freezing points. Thus the addition of iron to a certain point might lower both the sulphide and metallic lead content of the matte. This effect is illustrated by the fusions in Table 6, which were made by melting together commercial FeS (FeS containing metallic iron) with Cu_2S and lead in various proportions. The analyses are of the matte layer only. As Leitgebel noted, the addition of metallic iron beyond a certain point lowers the percentage of content of the lead but little, even if the addition in weight caused by the iron is overlooked.

Hagg[14] has made a more recent study of iron-arsenic alloys containing up to 56.9 per cent As than is given by the international Critical Tables or by Friedrich (ref. 10, 131). It was found that Fe holds about 5 per cent As in solid solution at room temperature. With increasing arsenic the first compound is Fe_2As. No Fe_3As_2 was revealed by X-rays; however, microscopic study indicated such a compound to be stable above 795° C., below which it breaks down to Fe_2As and FeAs.

TABLE 6.—*Effect of Addition of FeS Plus Fe to Amount of Lead Retained by Various FeS-Cu_2S-Fe-Cu Mixtures*

Fusion No.	Analyses, Per Cent, Computed to Total of 100				Percentage of Ingredients Present[a]					
					As Sulphides			As Metals		
	Cu	Fe	S	Pb	FeS	Cu_2S	PbS	Fe	Cu	Pb
1	62.2	0.0	15.8	22.0	0.0	77.9	0.7	0.0	0.0	21.4
2	57.8	5.2	17.8	19.2	8.2	72.4	1.5	0.0	0.0	17.9
3	52.5	11.3	18.4	17.8	17.8	59.1	0.0	0.0	5.3	17.8
4	46.6	17.3	20.5	15.6	27.2	52.6	0.0	0.0	4.6	15.6
5	41.9	23.3	21.6	13.2	36.7	40.7	0.0	0.0	9.4	13.2
6	36.0	29.9	23.2	10.9	47.1	29.8	0.0	0.0	12.2	10.9
7	29.0	37.3	22.9	10.8	58.7	7.4	0.0	0.0	23.1	10.8
8	20.6	45.4	23.3	10.7	63.7	0.0	0.0	5.0	20.6	10.7
9	13.6	52.2	23.3	10.9	63.7	0.0	0.0	11.8	13.6	10.9
10	7.0	60.1	22.7	10.2	62.1	0.0	0.0	20.7	7.0	10.2
11		66.0	24.9	9.1	68.2	0.0	0.0	22.7	0.0	9.1

[a] Computed by assuming Fe has first claim to S, then Cu, and last Pb.

According to Hofman[15], speiss having a composition that lies between Fe_2As and Fe_4As is fine grained and viscous when melted and is likely to keep the lead suspended. Speiss of the composition Fe_5As is moderately fusible and quite liquid when melted, and retains only a few shots of lead. On the other hand, speiss containing the proportion Fe_6As and higher in iron is supposedly as harmful as those containing less iron. (These statements do not entirely agree with present experimental work, where it was found that the least lead was retained in mixtures of the approximate proportion Fe_3As.) The structure of this speiss was found on microscopic examination to be mainly a eutectic between solid solution and Fe_2As, with a small amount of primary Fe_2As crystals.

Copper-lead-arsenic System

Of the three binary systems here involved, the copper-lead diagram is the most definitely established. Although various investigators have studied the lead-arsenic and copper-arsenic systems, there is still much room for debate as to the correct interpretation of their results.

The International Critical Tables [(1927) **II,** 414] show a simple diagram for the system Pb-As with two branches of the liquidus dropping from the fusion points of arsenic (825° C.) and of lead (327° C.) to a eutectic point at about 95 per cent As and a temperature of 288° C. No solubility was noted in the solid state. Heike[2] found the two elements freely soluble in the liquid state, while solid arsenic was completely insoluble in solid lead and crystalline lead only slightly soluble in crystalline arsenic. No chemical compounds were observed. The eutectic occurs at 288° C. and 8.25 atomic per cent, or about 3.1 weight per cent As. These results are confirmed by Pushin[16].

The Cu-As system has been studied by Bengough and Hill[17] and by Friedrich[18]. The diagram as determined by Bengough and Hill is reproduced in Fig. 16. The liquidus between 0 and 44 per cent As consists of five branches, along which the five phases α, β, γ, ϵ and η began to separate from liquid. The phase α can hold about 3 per cent As in solid solution at the ordinary temperature. A first eutectic point occurs at 21 per cent As, and its solidification temperature is 685° C. The constituents of the eutectic are the α phase and the β phase, which is considered to be the pure compound Cu_3As containing 28.3 per cent As. The branch of the liquidus along which the phase γ begins to separate from the liquid alloy is almost horizontal for a range of about 4 per cent; that is, until a concentration of 32.2 per cent As is reached. The composition corresponds to that required by the formula Cu_5As_2, and the authors adopt the view that such a compound does exist between Cu_3As and Cu_5As_2. The polymorphic change occurring at 710° C. is evidently an inversion of the compound Cu_5As_2, which follows the compound into its solid solutions in both directions. The ϵ phase is assumed to be Cu_5As_2, holding about one per cent of an unknown phase, x, in solid solution. The inversion at 305° C. appears to be a polymorphic change in the unknown phase x.

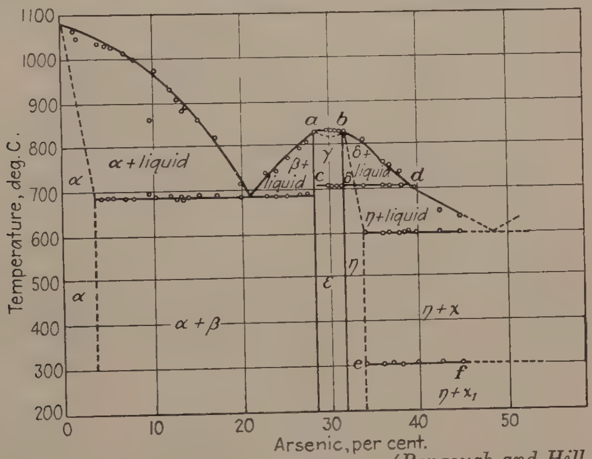


FIG. 16.—COPPER-ARSENIC SYSTEM. (*Bengough and Hill.*)

Another copper-arsenic diagram is given by Gulliver[19], which represents a composite of the works of Friedrich and Bengough and Hill. The arrangement of the diagram between 29 and 32 per cent As is disputed.

Gulliver adopted the view that only the compound Cu_3As separates at 830° C. As drawn, the transition at 305° C. represents a transition of the Cu_5As_2 phase, which has an incongruent melting point.

The interpretation of Fig. 16 as given by Bengough and Hill was roughly confirmed by fusing the copper and arsenic in the following proportions, cooling, and examining them under the microscope by the methods noted previously:

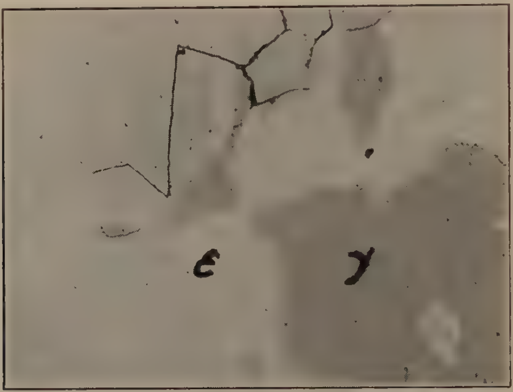


Fig. 17.—Transformation of γ to ϵ. As, 32.0 per cent. × 200.

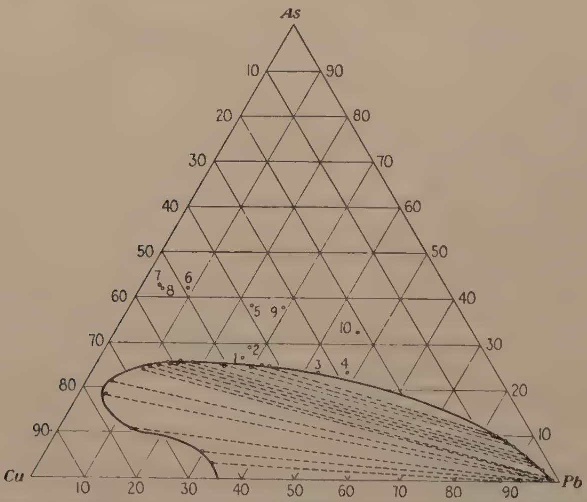


Fig. 18.—Copper-arsenic-lead system, showing area of immiscibility (two-layer systems).

Fusion No.	Percentages	
	Cu	As
1	94.3	5.2
2	70.0	29.1
3	67.6	32.0
4	62.3	36.4
5	61.8	37.2

The analysis and microscopic study of these alloys indicate that the compounds Cu_3As and Cu_5As_2 probably do exist. Under the microscope fusion 1 looks very similar to metallic copper. No. 2 consists only of a hard, bluish gray crystal. No. 3 consists of a hard unit substance, probably γ, which is usually at least partly transformed to a blue modification (Fig. 17). Fusions 4 and 5 consisted of primary white crystals in a eutectic that was assumed to consist of η and x.

For the investigation of the ternary system copper-lead-arsenic, thermal and microscopic analyses were made of 19 alloys lying within and 10 alloys outside of the immiscible areas. These results are summarized in Tables 7 and 8 and shown in Fig. 18. Fusions in which two layers occurred are designated by letter and are indicated in the diagram by open points, while those in which only one layer was found are designated by numerals and solid points.

All alloys of which the arsenical content did not exceed that required by the formula Cu_3As behaved identically under the microscope and thermally as pure copper-arsenic alloys, except that the freezing points were lowered somewhat by the presence of lead (alloys A to H). With more arsenic than is given by this composition, however, there appears to be considerable deviation both in thermal arrests and the microscopic appearance. Heats of transformation of the γ and x crystals probably were not strong enough for observation, since the melts contained only 35 grams of the alloy, about one-third of which was lead layer. γ, ϵ, α and η crystals were identified in these melts, and in addition a new kind of crystal (z) appeared (Fig. 22), which seemed to increase in importance with an increase in arsenic content.

The compound z, which probably has a platy crystalline habit, could not be definitely identified and may be either the compound x or some ternary kind of crystal. With the exception of z, all crystals are readily attacked by copper-ammonium chloride or nitric acid; z is slowly attacked. Lead always is segregated more strongly along the crystal boundaries of z, indicating a greater solubility of lead in this constituent.

SUGGESTED CHANGES IN THE DROSSING FLOWSHEET

Thus far, two main forms in which lead is retained in the matte-speiss product of the softening plant have been determined: (1) as lead sulphide and (2) as metallic lead in suspension or in solution in various sulphides and arsenides.

The presence of lead sulphide in matte-speiss (from plant B, Fig. 2) is undoubtedly largely due to the addition of much sulphur to the drossing reverberatory in the form of Hulst dross. The analysis of the Hulst dross (Table 1) shows that about 7 lb. of lead sulphide is drossed from the Hulst kettles for every pound of Cu_2S obtained, or about 84 per cent of the sulphur contained in the Hulst dross is combined as PbS. If copper could be removed from the bullion by the addition of less sulphur to the Hulst kettle, considerable combined lead could be kept out of the reverberatory. Also, if the copper could be removed from the bullion by some other method than by the addition of sulphur, even better results might be obtained in the reverberatory. The amount of arsenic

TABLE 7.—*Thermal and Microscopic Analyses of 29 Alloys within and without Immiscible Areas*

Fusion	Layers	Chemical Analyses, Per Cent[a]						Photomicrographs
		Upper Layer			Lower Layer			
		Cu	Pb	As	Cu	Pb	As	
WITHIN IMMISCIBLE AREAS								
A	2	61.4	31.2	3.3	11.1	87.5	0.4	
B	2	68.8	29.3	5.6	7.1	92.7	0.2	
C	2	73.1	13.2	10.5	4.2	95.5	0.3	Fig. 19
D	2	74.5	4.4	17.9	1.5	98.4	0.1	
E	2	73.5	4.8	18.0	1.4	98.4	0.2	Fig. 20
F	2	71.3	4.3	20.8	1.3	98.5	0.2	
G	2	63.8	10.0	24.4	2.0	97.2	0.8	
H	2	63.6	9.1	22.8	2.2	97.2	0.6	Fig. 21
I	2	61.2	12.8	24.9	2.1	95.3	2.6	
J	2	59.6	13.3	24.9	3.0	92.7	4.3	
K	2	59.0	13.6	24.6	2.8	92.0	3.8	
L	2	57.1	15.1	25.1	3.5	90.4	6.1	Fig. 22
M	2	57.4	15.0	24.5	2.6	92.9	4.5	
N	2	55.5	18.0	24.5	3.4	90.7	5.9	
O	2	49.4	23.6	24.1	4.9	85.9	7.6	
P	2	49.2	24.9	23.7	5.0	87.6	7.4	
R	2	44.5	28.5	23.9	5.8	84.0	8.5	
S	2	43.6	30.6	24.1	6.8	81.4	10.2	
T	2	42.4	33.0	24.0	7.6	80.8	10.1	
WITHOUT IMMISCIBLE AREAS								
1	1	45.9	26.4	25.4				
2	1	42.3	26.0	28.0				
3	1	33.2	42.2	22.6				
4	1	28.4	48.2	23.4				
5	1	37.5	22.4	36.3				
6	1	46.8	8.8	39.5				
7	1	51.5	2.9	40.3				
8	1	50.8	4.2	39.9				
9	1	31.1	27.0	36.2				
10	1	20.3	43.2	31.0				

[a] For critical points see Table 8.

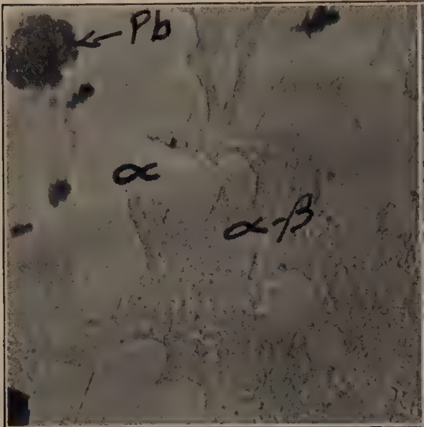
TABLE 8.—*Microscopy of Layers of Fusions of 24 Alloys*

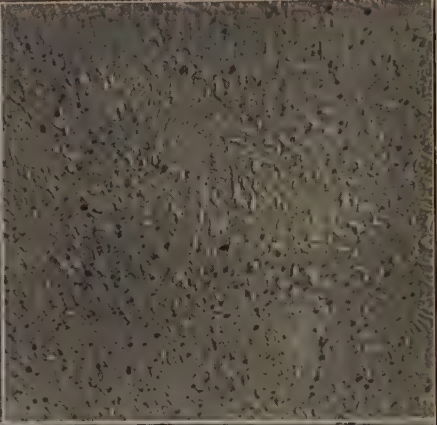
Fusion	Layers	Temperature, Deg. C., of Critical Points[a]				Microscopic Appearance	
		1	2	3	4	Upper Layer	Lower Layer
A	2	930	670		325	Primary *a* with lead in large drops. Also a small amount of *a-b* eutectic.	Lead with network of copper.
B	2	882	670		320	Primary *a* crystals in *a-b* eutectic. Lead associated mostly with *a* crystals.	The same.
C	2	812	670		320	The same with a larger amount of *a*.	The same.
D	2		670		325	*a-b* eutectic. Uniform distribution of lead in small drops.	Lead plus a small quantity of *a* crystals.
E	2		672		320	The same with a small quantity of *b*.	The same.
F	2	753	673		325	Primary *b* in *a-b* eutectic.	The same.
G	2	772	670		314	Primary *b* in *a-b* eutectic. Lead in *b* as large drops. Small drops in eutectic.	Lead plus *a* and *b* crystals.
H	2	805	670		323	The same.	The same.
I	2	787	570	410	280	*g* crystals partly transformed to *e*. Some lead as large drops within the crystals and considerable lead segregated along the crystal boundaries.	Lead with some *g* and *e*. Lead here is light brown.
J	2	780			290		
K	2	770			290		The same.
L	2	756	525		286	Mostly *e* with a small amount of *g*, plus an unidentified crystal *x*. Lead very soluble in the *x* crystals.	Lead plus *g*, *e* and *x* crystals.
M	2	792	580	420	288		
N	2	772	530		285		
O	2	758	510	412	280		The same.
P	2	750	510		290		The same.
R	2	750		405	290	Mostly *n* with a small amount of *d*, plus considerable *x*. Lead again segregated mostly along the crystal boundaries of *x* indicating greater solubility in this crystal.	Lead plus *n*, *d* and *x*.
S	2	722		401	290		
T	2	724		418	290		
1	1	720		408	285	The same.	The same.
2	1	675		455	287	The same.	The same.
3	1	725		410	290	The same.	The same.
4	1	680		416	285	The same.	The same.
5	1	570	514		280	*e* with some *g* crystals, and also some *x*. Lead again segregated around *x* crystals.	Lead plus *e*, *g* and *x*.

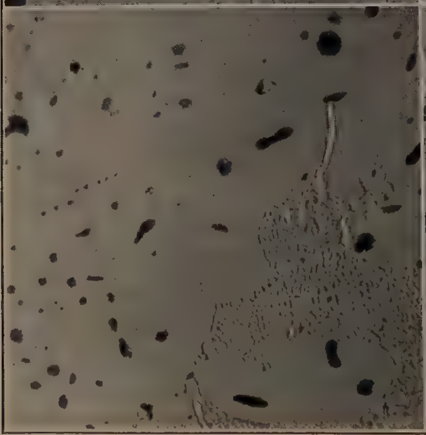
[a] Column 1 corresponds to the segregation of primary crystals.
Column 2 corresponds to the segregation of eutectic or binary mixtures.
Column 3 probably represents a ternary eutectic.
Column 4 corresponds to the freezing of the lead layer.

plus sulphur should, however, suffice to satisfy the copper as copper arsenides and sulphide.

As shown, although lead is soluble in iron sulphide, usually there is not much of this compound present, particularly when metallic iron is not added in treating drosses. Practically all of the lead retained as metallic lead in matte-speiss products containing little iron may be attributed to the solubility of lead in copper sulphide and, more especially, in the various copper arsenides in the liquid state. The amount of lead thus soluble is a function of the composition and amount of the sulphide or arsenide involved. It has been shown that the amount of metallic







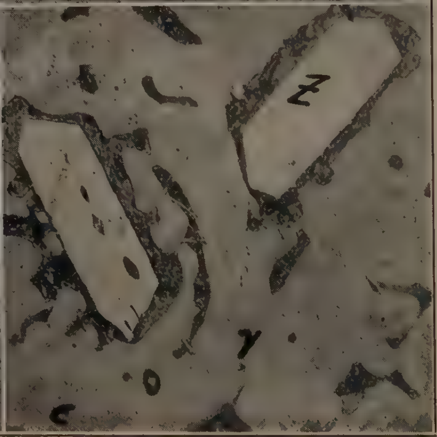


Fig. 19.—Polished section of fusion C. × 200. Showing primary α crystals in α-β eutectic. Dark areas are metallic lead. (Table 6.)

Fig. 20.—Fusion E α-β eutectic with lead distributed throughout in very small drops. × 200. (Table 6.)

Fig. 21.—Fusion H. Primary β with small amount of first eutectic. Dark areas, metallic lead. × 200. (Table 6.)

Fig. 22.—Fusion L, γ partly transferred to ϵ and also Z. Note segregation of lead around the Z crystals. × 200. (Table 6.)

lead soluble in Cu_2S may be lowered by the presence of certain amounts of either PbS or FeS, one or both being nearly always present.

Two main factors present themselves in the consideration of this problem; first, the amount and form of combination of the copper, and, second, the amount of arsenic that reaches the base bullion. If the ratio of copper to arsenic that reaches the dross could be raised, less lead should be retained, since up to certain ratios (Table 9) copper arsenides containing a smaller percentage of arsenic dissolve less lead. There should be between 3.4 and 4.1 per cent Cu present for each 1 per cent As. Particular attention is called to the photomicrographs in connection with the table. The relative amounts of lead retained by the various copper arsenides may not only be checked against the chemical analyses but the manner in which the lead is retained in each sample is also clearly shown.

TABLE 9.—*Amounts of Metallic Lead Retained by Alloys Containing Varying Proportions of Copper and Arsenic*

Arsenide	Cu-As Ratio	Pb, Per Cent	Photomicrograph	Arsenide	Cu-As Ratio	Pb, Per Cent	Photomicrograph
A	18.6	31.2		K	2.4	13.6	
B	12.3	29.3		L	2.3	15.1	Fig. 22
C	7.0	13.2	Fig. 19	M	2.3	15.0	
D	4.1	4.4		N	2.2	18.0	
E	4.1	4.8	Fig. 20	O	2.0	23.6	
F	3.4	3.4		P	2.1	24.9	
G	2.6	10.0		Q	1.8	28.5	
H	2.7	9.1	Fig. 21	R	1.8	30.6	
I	2.5	12.8		S	1.7	33.0	
J	2.4	13.3		Matte-speiss	2.0 to 2.3	19 to 27	

The percentages of lead given in Table 9 are those soluble in the various copper arsenides at temperatures just above the freezing points and could be expected to increase materially with a rise in temperature. Thus, even though the lead smelter should succeed in obtaining the correct Cu-As ratio for the speiss in the drossing reverberatory by removing more of the arsenic in the sintering operation, the common method of granulating the speiss in tapping this liquid from the reverberatory would cause considerable lead to be retained in the quenched product. The amount of lead retained may be decreased by tapping into pots, freezing the arsenide, and finally separating the still molten lead from the speiss layer. By this means it should be possible to obtain a rich product from the copper reverberatory containing only 4 to 6 per cent Pb.

The amount of copper and arsenic in the dross might be lessened in one of several ways:

1. It has been pointed out as a metallurgical possibility that copper and arsenic may be removed as a separate concentrate in milling some

lead ores[20] in which copper and arsenic occur mainly as minerals in the tetrahedrite-tennantite series.

2. More of the arsenic might be volatilized during the sintering operation by the addition of pyrite or coke to the regular sinter charge, perhaps by giving the sintered cake a third pass over the Dwight-Lloyd machines.
3. It might be possible to crush and roast either part or all of the final speiss product with pyrite, and thus remove enough arsenic so that upon remelting (perhaps with a little reducer) at least part of the lead would be liquated out.

The roasting of copper, iron, and nickel arsenides has been described by Tafel and Loose[21]. In this process the removal of arsenic is attributed partly to the reducing action of SO_2 and partly to the decomposition of arsenates and arsenites by SO_3. It is also thought that such volatile compounds as As_2S_3 are formed. These points were checked experimentally by roasting a copper speiss with various mixtures of pyrite, charcoal, sulphur and SO_2. Arsenic was roasted off most effectively by the addition of sulphur in some form.

Effect of Precious Metals upon Drossing Practice

The distribution of the precious metals among the products made in drossing may greatly influence the scheme of drossing followed. For instance, it is usually desired to throw the precious metals with the lead bullion, and to keep them out of the matte and speiss. It is also desired that the antimony be kept in the bullion when the latter is to be refined by the Betts process.

In an attempt to reduce the metallic lead retained in the reverberatory products by increasing the copper-arsenic ratio, it was found that the unsatisfied copper combined with the antimony of the bullion; in fact, antimony might be drossed from bullion by adding copper. The copper antimonide formed dissolved much of the gold from the bullion, as noted in the following analyses of matte-speiss from the drossing reverberatory:

	OZ. PER TON		ANALYSES PER CENT						APPROXIMATE WEIGHT OF PRODUCT MADE, TONS
	AU	AG	CU	PB	AS	SB	S	FE	
Matte........	0.16	15.6	64.6	12.0	0.7	1.0	15.8	0.2	4
Speiss.........	10.48	59.7	58.4	15.6	7.4	11.4	0.7	0.3	6

Under the microscope, the matte sample showed mainly Cu_2S, with some metallic copper and metallic lead in small drops, apparently squeezed out of the Cu_2S melt upon solidification. No sulphide lead was found. The speiss sample showed Cu_3Sb, together with copper arsenide and metallic lead. No metallic copper was noted.

Thus, when the precious-metal content of the matte-speiss product is of no consequence, a comparatively high-grade product may be produced by decreasing the sulphur and arsenic content of the reverberatory charge. When the gold and silver content of the product is important, the rich-lead, poor-gold speiss originally produced might be roasted and remelted in the absence of antimony to liquate out some lead.

SUMMARY

It is obvious that the amounts of copper, arsenic, and sulphur compounds fed to the blast furnace should be as small as possible without overbalancing economic losses. It saves handling of impurities to remove them as early as possible in the metallurgical flowsheet. The following places suggest themselves:

1. *Concentration.*—Minerals of copper and arsenic may be removed from some ores in the concentrator. If so, this is the best place to remove them.

2. *Roasting.*—Arsenic may be most readily volatilized in the roasting operation. Arsenical compounds do not volatilize rapidly from the Dwight-Lloyd machines when coke is not added to the charge. It is indicated that hearth furnaces are more effective for this purpose. Arsenical compounds volatilize more rapidly when heated with sulphur, pyrite, or coal. Arsenic may be removed from flue dust, returned crushed speiss, etc., by roasting with such reducers in a furnace of the Wedge type.

3. *Blast Furnace.*—An open and porous charge and conditions to produce As_2O_3 within the furnace assist to volatilize the arsenic most rapidly. But little arsenic is likely to volatilize after metallic lead is liquating out freely. Iron and sulphur assist as reducers. Iron replaces lead from the sulphide and, by forming speiss with the arsenic, keeps this ingredient out of the bullion. (Too much iron in the basic slag may combine with enough arsenic and sulphur to put copper in the bullion.) Copper also takes up arsenic, although it is another impure product to be handled, and once it enters the blast-furnace charge it may thus help to make cleaner bullion.

4. *Dross.*—Speiss may be returned to a hearth roaster to remove the arsenic. The use of the drossing reverberatory was developed as an improvement over concentrating the copper content of mattes by reroasting and resmelting.

5. *Nature of Lead Drosses.*—The compounds present in the softening plant dross, matte and speiss are: Lead sulphide, cuprous sulphide, solid solution of cuprous sulphide plus ferrous sulphide, copper arsenides (Cu_3As_2 + Cu or As), metallic lead and metallic copper. Other compounds not positively identified are probably iron arsenide and copper antimonide.

6. The presence of metallic copper in the matte is probably due to the reaction between copper sulphide and iron sulphide to form moss copper. Mattes that do not contain iron do not contain metallic copper.

7. Considerable lead is retained by cuprous sulphide or by lead sulphide. Cu_2S-PbS and Cu_2S-FeS mixtures do not retain as much metallic lead as do the pure sulphides.

8. The main part of the metallic lead retained by the matte-speiss products is suspended in copper arsenides, chiefly in Cu_5As_2.

9. *Removal of Lead in Drossing Reverberatory.*—The quantity of lead retained in the sulphides of the matte-speiss from smelter B was about the same without metallic iron or with as much as 10 per cent. When metallic iron was added to various synthetic mixtures, the content of metallic lead was not lowered by adding iron beyond a certain percentage.

10. The products in the reverberatory do not need to remain molten over an hour. The cleanest separations of products may be made by allowing them to solidify slowly and then separating the various layers, rather than by granulating molten speiss or matte products.

11. A mixture containing about 3.5 parts of copper to 1 part of arsenic retained the least amount of metallic lead. The formation of speiss of this composition is not possible in the presence of bullion containing antimony.

12. The formation of copper antimonides is to be avoided, especially at plants not having copper smelters, because gold and silver are quite soluble in these compounds.

Acknowledgments

The authors take this opportunity of acknowledging the assistance of the staffs of all the lead smelters near Salt Lake City, and especially thank Mr. Gerald U. Greene for furnishing data on plant flowsheets. Mr. Robert Wallace, metallurgist for the United States Smelting, Refining & Mining Co. at Midvale, Utah, was particularly helpful in supplying samples and offering suggestions. Mr. R. E. Head, microscopist for the Metallurgical Division of the U. S. Bureau of Mines, also contributed suggestions in his field.

References

1. M. N. Short: Microscopic Determination of the Ore Minerals. U.S. Geol. Survey *Bull.* 825 (1931).
2. W. Heike: The Equilibrium Diagram of Lead-arsenic Alloys and the Melting Point of Arsenic. *Int. Ztsch. f. Metallog.*, **6,** 49–57.
3. K. Friedrich: Investigation of Layer-forming Systems. *Metall und Erz* (1912) **10,** 575, 976.
4. H. O. Hofman: Metallurgy of Copper, 15. New York, 1914. McGraw-Hill Book Co.
5. K. Friedrich and A. Leroux: Lead and Sulphur. *Metallurgie* (1905) **2,** 566.
6. K. L. Meisner: Equilibrium between Metal Pairs and Sulphur, I—The System Copper-lead and Sulphur. *Metall und Erz* (1921) **18,** 145.
7. C. H. Fulton and I. E. Goodner: Constitution of Copper-iron and Copper Lead-iron Mattes. *Trans.* A.I.M.E. (1905) **36,** 665.

8. W. Leitgebel: Considerations of Theoretical Metallurgy—the System Pb-Fe-S. *Metall und Erz* (1926) **23**, 439.
9. Weidmann: Bleistein. *Metallurgie* (1906) **3**, 660.
10. K. Friedrich: Galena and Pyrrhotite. *Metallurgie* (1907) **4**, 480.
11. C. B. Carpenter and C. R. Hayward: The Equilibrium Diagram of the System Cu_2S-FeS *Eng. & Min. Jnl.* (1923) **115**, 1055.
12. H. Tiedemann: Formation of Moss Copper in Copper Mattes. *Metall und Erz* (1925) **23**, 200.
13. O. Reuleaux: Reactions and Equilibria in the System Copper-iron-sulphur with Reference to Copper Ores. *Metall und Erz* (1927) **24**, 99.
14. G. Hagg: An X-ray Study of the System Fe-As. *Ztsch. f. Krist* (1929) **71**, 134–136.
15. H. O. Hofman: Metallurgy of Lead, 296. New York, McGraw-Hill Book Co.
16. N. A. Pushin: Potential and Nature of Metallic Alloys. *Jnl.* Russ. Phys. Chem. Soc., **39**, 869–897.
17. G. D. Bengough and B. P. Hill: Properties and Constitution of Copper-arsenic Alloys. *Jnl.* Inst. Metals (1910) **3**, 34.
18. K. Friedrich: *Metallurgie* (1908) **5**, 529.
19. G. H. Gulliver: Metallic Alloys, 286. London, 1913. Charles Griffin & Co.
20. R. E. Head, A. L. Crawford, F. E. Thackwell and G. Burgener: Microscopic Analysis of Silver King Ores and Mill Products. U. S. Bur. Mines *R.I.* 3236 (1934).
21. V. Tafel and H. W. Loose: Reactions in Removal of Arsenic from Speiss by Heating in Presence of Pyrites. *Metall und Erz* (1931) **28**, 422–425.

Treating Blast-furnace Drosses

By O. P. Chisholm,* Member A.I.M.E.

Development in Use of Dross Reverberatory Furnace

Dross emerges from the blast furnace either with the lead through a lead well or by tapping from a forehearth or settler, but until a dozen years or so ago few dross reverberatories were used in western lead smelters because it was the usual procedure to circulate the dross from the drossing lead kettles back to the blast furnace.

It was quite customary for lead smelters to produce matte in their blast furnaces, as this was the form in which copper could be collected, concentrated if necessary, and shipped to the copper smelters for further treatment. The main prerequisites for good matte formation are, of course, a more or less definite amount of copper on the charge and sufficient sulphur. Such troublesome impurities as arsenic and antimony were ignored, in so far as possible, although they contaminated the bullion and thereby increased refinery costs. At the same time stocks of blast-furnace speiss containing gold, silver, lead and copper in addition to iron, arsenic and antimony, were being accumulated for want of a market to absorb them. As the dross was being fed back to the furnaces as rapidly as it was being produced, arsenic and antimony tended to build up until the arsenic could effect a combination with copper and iron and an alliance with lead, and the antimony a combination with copper and an alliance with lead. Sulphur, being the most active agent in taking up the copper, left little of that element for the arsenic and antimony, so that on the whole a somewhat unsatisfactory metallurgy resulted.

During this same period, certain lead plants were beginning to encounter trouble with zinc due to the replacement of crude ores of low zinc content by concentrates containing high percentages of lead and zinc in sulphide form, the blast-furnace slags resulting from the smelting of such concentrates being characterized by a decidedly increased zinc content. It was soon realized that zinc plus sulphur was "poison" to a lead blast furnace and steps were taken to reduce the sulphur content. At this stage some plants found that any substantial matte fall was out

---

Manuscript received at the office of the Institute July 29, 1936.

* Superintendent, East Helena Plant, American Smelting and Refining Co., East Helena, Mont.

of the question because of the relatively small amounts of copper and the abundance of zinc, so that with the gradual perfection of double sintering to a point where there was no tendency to form matte, the situation became one in which only the dross was left as the copper carrier, except for the copper lost in the slag.

However, certain plants still adhered to the blast furnace as a means for producing matte from the dross by the running of so-called "hot charges" between regular furnace charges, a hot charge being, as its name implies, "hot," and usually consisting of equal weights of dross and blast-furnace slag to which was added a certain amount of sulphide ore (preferably pyrite) and small amounts of siliceous ore, limestone, scrap iron and coke. While this procedure was fairly satisfactory at a plant producing a relatively low-zinc slag, and where the ratio of arsenic and antimony to copper was low, it was by no means satisfactory at plants where high zinc prevailed, because the zinc combined with the sulphur of the pyrite to form "zinc mush" (ZnS), which not only had a refractory nature but also served to increase metal losses in the slag.

The substitution of the dross reverberatory for the blast furnace eliminated the necessity for any considerable amount of slag formation, always associated with blast-furnace practice. In the reverberatory operation it is advantageous to produce a fluid slag relatively free from entrained metals, particularly copper, but the composition need not adhere to close fluxing limitations for successful operation. As the slag from the dross reverberatory ordinarily is retreated either in a lead blast furnace or in a copper reverberatory, it is considered good practice to produce as little slag as is consistent with sufficient fluidity.

The first dross reverberatories operated in the West, at Selby and East Helena, were matte-making furnaces. No attempt was made to regulate the fluxing to assure a high copper to lead ratio in the matte tapped from the dross charge, as the better ratio was secured by remelting the "first" matte and adding scrap iron and silica in what was termed a "concentration" run. Quite satisfactory results were obtained in this manner but the process had the disadvantages of the extra handling and increased fuel. A little later a similar operation was practiced at East Helena except that arsenic, rather than sulphur, was the principal collecting medium for the copper. After a period of experimentation, the double treatment was replaced by one operation, which produced a speiss of fair copper to lead ratio. Following the experience at East Helena, the use of dross reverberatories became a part of the usual operations at Chihuahua, Durango, El Paso, Murray and San Luis. The Durango furnace was purely a matte-making furnace while the one at El Paso produces mostly matte and some speiss. At present the others are employed primarily in speiss-producing operations.

TABLE 1.—*Construction Features of Dross Reverberatory Furnaces*

	East Helena	Selby	Murray	El Paso	Durango	Chihuahua	San Luis
Hearth size, inside measurement, ft.	7 × 21 7 × 28	6 × 22	7 × 21	8′ 9″ × 27′ 7″	7 × 18	7 × 21	7 × 21
Wall thickness, in.: at bath	18	13	18	18	18	18	9
Above bath	18	13	18	9	18	9	9
Bottom inverted arch, in.	13½	11½–18½	9	18	9	9	9
Below invert	Concrete	Concrete	Brasque	Cushion fill	Concrete	Concrete	Concrete
Invert	Firebrick	Firebrick	Firebrick	Firebrick	Firebrick	Firebrick	Firebrick
Bath walls inside	Magnesite	Magnesite	Magnesite	Firebrick	Magnesite	Magnesite	Magnesite
Wall above bath	High alumina inside	Alumina	High alumina	High alumina	High alumina	High alumina	High alumina
Arch	High alumina	High alumina	High alumina	High alumina	High alumina	High alumina	High alumina
Charge hole in arch	Water-cooled cast-iron ring	Side doors	Water-cooled cast-iron ring	Water-cooled copper cast	Water-cooled cast-iron ring	Water-cooled cast-iron ring	Water-cooled cast-iron ring
Shape hole	Round	None	Round	Square outside	Round	Round	Round
Depth of bath, in.	20–24	16½	32	36	24	28	30
Lead tap	Lead well side furnace	Side tap	Side tap	End tap	Side tap	End tap	End tap
Fuel used	Natural gas	Natural gas	Natural gas	Natural gas	Natural gas	Fuel oil	Fuel oil
Capacity in 24 hr., tons	60–90	30–50	60	150	50	80	80

FURNACE CONSTRUCTION

Among the furnaces included in Table 1, the smaller one (7 by 21 ft.) at East Helena, Mont. (Fig. 1), was designed after an examination of an earlier reverberatory furnace used at Selby, Calif., which was the pioneer among western smelters in making matte from blast-furnace dross. East Helena developed the idea of forming copper-bearing speiss from dross until the exclusion of matte formation was accomplished. Later Murray, Chihuahua, Durango, San Luis and El Paso built dross reverberatory furnaces (Figs. 2 and 3). The furnace at East Helena influenced the design of the later furnaces, although, as may be observed from the tabulation, many changes have been made either on account of local conditions or with an eye to improvement.

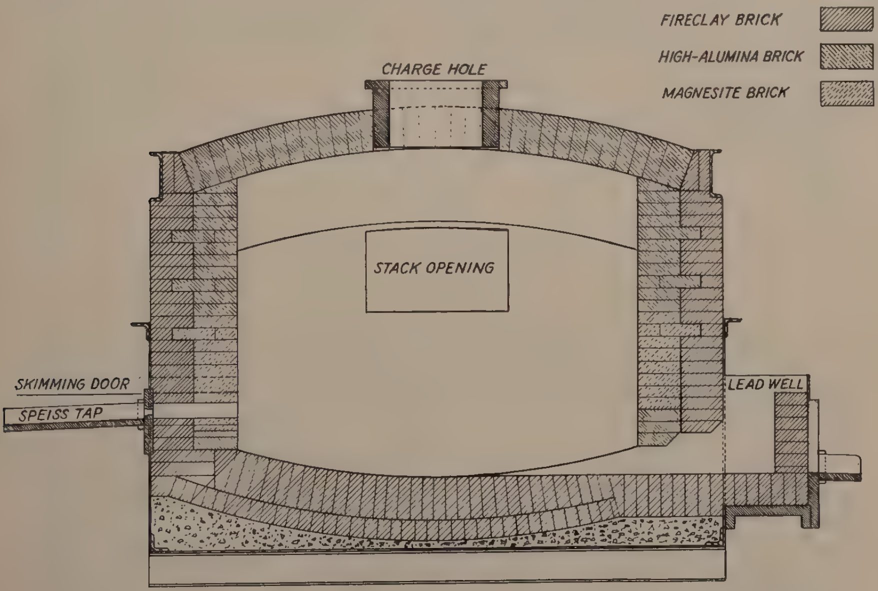


FIG. 1.—CROSS SECTION OF DROSS REVERBERATORY AT EAST HELENA.

East Helena still adhered to the lead well for tapping lead which, while it has the advantage of lessening the possibility of a "runaway," has the disadvantage that it is difficult to open if the channel "freezes." There is also a horizontal channel in this furnace reaching to the center of the inverted arch, for tapping when the furnace must be emptied preparatory to a shutdown. Most furnaces have lead taps on the side, the bullion being caught in cast-iron pots or brick-lined steel pots of about 3000 lb. capacity. At El Paso and in Mexico the lead taps are flush with the top of the inverted arch at the burner end of the furnace and bullion is tapped into a launder leading to a large drossing kettle. The operating advantage of this arrangement, over that at plants where it is necessary

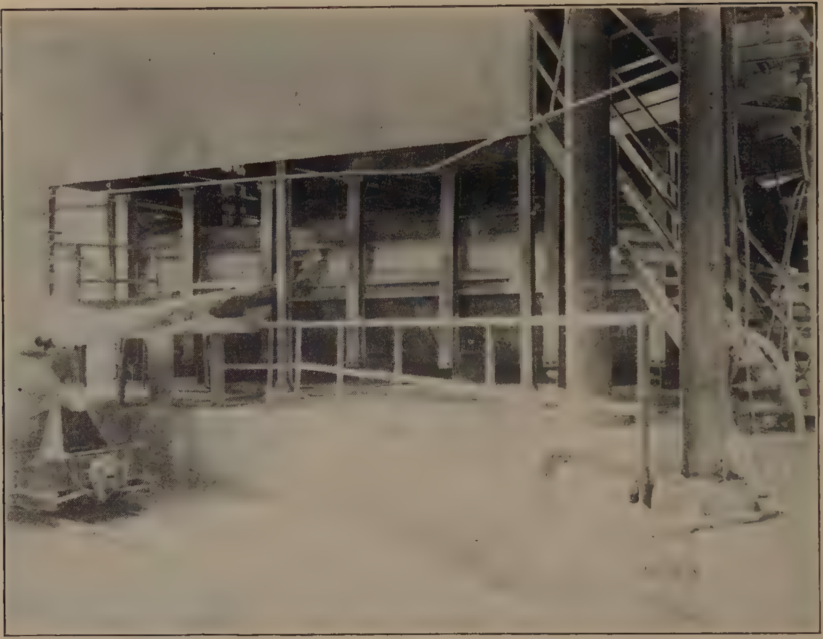


FIG. 2.—SIDE VIEW OF DROSS FURNACE AT EL PASO.

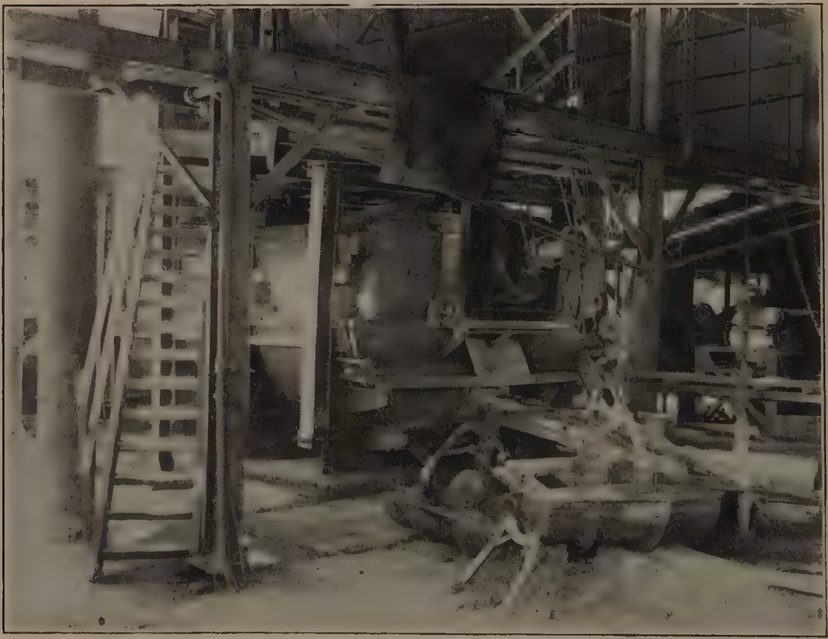


FIG. 3.—END VIEW OF DROSS FURNACE AT EL PASO.

to tap the lead intermittently and then tram and hoist it to drossing kettles, is obvious.

All furnaces have a steel pan surrounding the brickwork of the bath, the top of the pan usually being at the level of the slag-skimming bay. The pan ordinarily rests on I-beams 6 in. high, suitably spaced to allow air to circulate beneath the pan, a condition that has been found desirable. The butt joints are riveted and at some plants welded in addition. Welding without riveting has been tried and in at least one instance proved unsatisfactory, as expansion of the brickwork exerted too great a force and caused failure at the joints.

In laying up the brickwork allowance is always made for expansion. At one plant 1½ in. of space allowed at each end of the inverted arch, between arch and steel pan, is filled with dry fireclay. For side and end walls, where the outside course is firebrick, wooden strips 9 by 2½ by 3⁄16 in. are used every 4 ft. for expansion allowance. For the magnesite inside lining of the walls, wooden strips of the same size are used every 12 in. When high-alumina brick are used for walls, the wooden strips are used every 4 ft. Along the arch longitudinally a 3⁄16-in. expansion joint is allowed at each end between arch and end wall for approximately every 10 ft. of furnace length. Sometimes strips of roofing material are used instead of the wooden strips.

Most of the furnaces are rectangular with inverted arch sprung crosswise, vertical side and end walls, and an arch roof sprung crosswise. At Selby the spring in the inverted arch is longitudinal with the lead tap at one side of the furnace. The furnaces are usually bound with vertical buckstays placed at the sides of the furnace, the lower ends of the buckstays being set in concrete and the tops held by adjustable tie rods. In some installations tie rods are used at the bottoms of the buckstays.

The charging holes are usually lined with a water-cooled cast-iron ring. A shallow cast-iron hopper is placed above the ring to act as a receptacle for catching the charged material and directing it to the charge hole. At El Paso a cast copper ring containing coils for water circulation is used. The outside contour is square, which is simpler from the bricklaying point of view. In most cases the charge hole is sealed with a cast-iron tapered plug suspended from a steel cable, the plug being removed during charging and replaced thereafter. Sometimes compressed air is used for actuating the movement. At one plant, where an unusually large charging hole is used, the hopper is dispensed with and a brick cover, bound at the edge with steel bands and stiffened with steel rods, is used successfully.

An improved furnace at El Paso differs from the typical dross reverberatory in that the pan is not resting on I-beams placed in the conventional manner but, being semicircular in cross section, it is supported in cradle fashion, upon superimposed I-beams cut to fit. Between the

TABLE 2.—*Handling Equipment*

Plant	East Helena	Selby	Murray	El Paso	Durango	Chihuahua	San Luis
Charge container	Skip	Tram car	Skip	Skip	Skip	Skip	Skip
Charge hoist	Electric trolley	Hand shoveled	Electric trolley	Electric crane	Electric crane	Electric crane	Electric crane
Slag disposal	Small pots	Small pots	Large pots	Large pots to copper reverberatory	Large pots	Large pots	Large pots
Matte or speiss	Granulated for shipment	Granulated for shipment	Granulated for shipment	Large pots to converter	Granulated for shipment	Granulated for shipment	Granulated for shipment
Bullion	Pots	Pots	Pots	60-ton kettles	Pots	110-ton kettles	50-ton kettles

circular pan and the first course of brick is a 2-in. cushion fill. Two courses of brick on end, or 18 in. in all, form the bottom and sides of the bath portion. The side walls above the bath are 9 in. thick. The arch is independently supported from steel channel skewback supports, which are fastened to the side buckstays rather than being sprung from a skewback supported on the outer brick course of the side walls, as is the usual arrangement.

The gases exit through a throat at the end of the furnace opposite the burners, into an uptake and thence through a flue. The fume usually is filtered by means of a baghouse, which also filters gases from the blast furnaces. The Durango reverberatory gases were treated successfully by the Cottrell process along with blast-furnace gases. At Durango, there is an uptake over the furnace bath and slag skimming is done by rabbling through a skimming bay at the end of the furnaces. Other furnaces have the skimming bay at one side of the furnace, usually near the throat. Matte and speiss taps are on the side of the furnace. Tapping blocks are usually made of cast iron and in some instances are water-cooled. At El Paso, copper tapping blocks have been used successfully.

A good grade of firebrick is used for the inverted arch while magnesite brick is used for bath-wall linings, usually backed up with firebrick. High-alumina brick is used for side walls above the bath and for the arch. With an 18-in. side wall above the bath, the outside course is usually built of firebrick.

Of the plants mentioned in this article, five use natural gas for fuel and two use oil; the gas burners vary with locality and conditions. A single long-flame burner has been used successfully on the 28-ft. furnaces, whereas several small short-flame burners have proved more effective and economical on some of the 21-ft. furnaces. The long-flame burners are of the inspirator type; the smaller ones are of the refractory type of atmospheric burners with fluted fireclay blocks.

The fuel oil used is 13° Bé. From two to three burners are employed, accurately pointed through the bridge wall so that the flame will strike the charged material at a point slightly above the molten bath level. Air is taken from the air-blast line running to the blast furnaces.

Handling Equipment

After the molten bullion, which comes from the blast-furnace lead well or settler, has been delivered to the drossing kettles, which usually hold 30, 60 or 110 tons, the appearance of dross is noted. Contrary to the usual significance of the term to the layman, this dross is a valuable product, being usually enriched with gold to a greater extent than the "clean" bullion itself. Removal of the dross begins when the kettle is filled and is usually performed by skimming with a perforated ladle to which is attached a substantial handle. A chain is fastened to the handle and the whole suspended from a roof truss above the kettle. The receptacle for receiving the dross may be a perforated basket floating on the bath or it may be a skip or boat resting at the edge of the kettle. When filled, the basket is hoisted clear of the bath and allowed to drain before delivering its contents to the dross reverberatory furnace or stockpile. The skip or boat is tilted so that the clean molten lead will flow back to the kettle. Obviously, it is good practice to retain as much clean lead as possible in the kettle.

Some plants for years have produced a "dry" dross on the kettles before skimming, by using a bullion stirrer, which consists essentially of a motor-driven impeller. As the impeller blades, set 2 or 3 ft. below the surface of the bath, revolve about a vertical shaft, a rotating motion is given to the molten bath, which creates a vortex in the vicinity of the shaft. In operation, an observer may witness the travel of the dross as it is drawn spirally into this vortex and rises to the surface of the bath near the rim of the kettle. After a time a noticeable change takes place in the appearance of the dross, in that, from a mass of lumpy substance matted together with metallic lead, it becomes dusty in appearance and somewhat resembles a dry concentrate. It contains all the constituents it had before stirring but its lead content is much lower, so that the treatment is advantageous in that it reduces the tonnage of dross to be subsequently smelted in the reverberatory.

Delivery of the dross to the furnace is by overhead electric trolley hoist or crane. When delivery is made to stockpile it is usual to dump the dross on a plate, where it is moistened and separated by shovel before piling. For a "dry" dross the wetting and separating by shovel may be dispensed with.

Bullion is tapped into pots and trammed and hoisted to drossing kettles, or it may be tapped directly into drossing kettles if the plant is so arranged.

Slag is skimmed through a bay from the furnace into pots and after cooling is broken with a sledge and sorted to recover entrained matte or speiss. The slag is returned to the blast furnace and the sorted matte or speiss is shipped to a copper plant if its quality warrants.

Matte and speiss are tapped from the side of the furnace into a launder or spout, which conveys the molten stream to a granulator. A suitable pit is provided from which the accumulated material may be recovered for shipment at the conclusion of the tap. Provision is made in the granulating pit for drainage of the water without loss of the product.

Cycle of Operations

Although the operating routine varies from plant to plant, owing to handling equipment and local conditions, there is a similarity in procedure. After the furnace has been charged and the molten bath is of sufficient depth, the slag is skimmed. Lead may be withdrawn while charging and melting is in progress. Before matte or speiss is tapped, the depth of the lead is usually measured by inserting a bar into the molten bath and withdrawing it for inspection, to determine the height of the lead in relation to the matte or speiss tap-hole. The lead must be drawn down low enough so that no lead or fused dross can emerge from the matte or speiss tap-hole. When a satisfactory condition is established, the matte or speiss may be tapped.

The El Paso plant taps the matte and speiss into large pots, which are hauled to copper converters and charged while in the molten state. The other plants referred to in this article granulate the matte or speiss, supplying sufficient water and sufficient pressure at the water nozzle, where the molten stream of matte or speiss meets the water, to prevent explosions. In practice, with a given volume of water and pressure available, the control has resolved itself into regulation of the flow of the molten matte or speiss delivered to the granulator. Granulation has the advantage over the old practice of casting the speiss into thin cakes, in that it eliminates the excessive crushing costs necessitated by the old practice to condition it for further treatment in the copper smelter. Further, the granulated product may be readily and accurately sampled.

The Process

At certain plants the process of producing copper-bearing speiss from dross is mainly one of liquation of the lead. This presupposes, however, a condition that is rarely encountered in practice; namely, a suitable copper to arsenic ratio so that little or no fluxing is required. Accordingly, various practices are employed at the different plants to cope with the existing local conditions and obtain a product or products best suited to their individual situations.

At one plant, neither scrap iron nor blast-furnace speiss is used, the charge to the dross reverberatory comprising only dross, a small amount of siliceous oxidized ore and a little limestone. Of the material tapped, about one-quarter is almost equally divided between matte and speiss while the other three-quarters is principally speiss analyzing well over 50 per cent copper.

In contrast to that operation is one at another plant where the charge is approximately one-quarter blast-furnace speiss with a small amount of siliceous ore in addition to the dross. The product is a speiss with a very desirable copper to lead ratio but with a much lower copper content than the speiss obtained in the first operation mentioned. The metallurgist in charge at this plant attributes the excellent copper to lead ratio to the maintenance of strong reducing conditions and use of sufficient scrap iron in the blast furnace producing the dross.

At another plant, the usual charge contains, in addition to the dross, small percentages of siliceous ore and limestone and scrap iron from which a copper-bearing product comprising a mixture of matte and speiss, with the latter predominating, is obtained. The metallurgist in charge states that the addition of the scrap iron, up to a certain percentage, apparently exerts a slightly beneficial effect; above that it merely dilutes both the copper and the lead.

At still another plant, it has been found, in a general way, that for a particular copper content the better copper to lead ratio can be secured by incorporating proper quantities of blast-furnace speiss, and in certain instances, scrap iron, in the charge. Generally speaking, they have observed that the copper and lead contents of the speiss rise as the arsenic and iron contents, respectively, diminish.

However, it does not follow that the addition of iron alone will always lower the lead content because it is also influenced by the amount of arsenic present. Generally speaking, a poor ratio of copper to lead in a speiss of unusually high arsenic content can be bettered by the addition of scrap iron to the charge or by reducing the amount of common speiss charged (thus reducing the amount of arsenic) and using scrap iron. With a speiss of lower arsenic content and having a poor copper to lead ratio, the ratio may be improved by the addition of common speiss to the dross reverberatory charge, although the copper content of the resulting speiss will be lowered to some extent.

The writer believes that the addition of blast-furnace speiss to the charge does more than simply dilute the copper and lead. Although no chemical reactions may be involved, beneficial results are obtained with respect to the copper to lead ratio. In this connection, Gerald U. Greene states[1] that the addition of common iron speiss "only serves to form a fluid bath" and that "since lead has practically no solubility in iron arsenide, some of the retained lead may be removed from the speiss by its addition"

---

[1] G. U. Greene: Thesis. A similar statement appears on page 186, this volume.

A Study of Drosses from Lead Blast Furnaces

By Gerald U. Greene*

(New York Meeting, February, 1935)

The various lead producers have given the subject of lead drosses much attention in recent years but the problem of their economical treatment is yet to be solved.

Formerly the copper in the furnace feed was removed from the furnace in the form of matte. The speiss at that time consisted principally of the iron arsenide. The practice today is to roast off most of the sulphur and the copper in the feed forms a dross in the furnace, which is removed from the furnace with the lead. This material is poured into the drossing kettles and allowed to cool down to but slightly above the freezing point of lead. The copper dross, containing almost all of the arsenic and part of the antimony, is skimmed off and treated in a small reverberatory furnace at most plants. This is essentially a liquation process. The skimmed dross contains from 70 to 80 per cent lead, and much of this lead is liquated out. The products from this treatment are: (1) impure lead, (2) speiss and (3) matte. The speiss from the reverberatory furnace was studied in this research.

The literature on the subject is of very little assistance, as almost no work has been done on the problem of establishing the exact identity of the various phases present. One author(1)† states that speiss consists of a series of isomorphous compounds of the general formula Fe_xAs_y in which the Fe may be replaced by Ni, Co, Cu, Pb, Ag, Au, Pt, Zn, Cd and the As replaced by Sb, S and Bi. Hofman(2) states that the iron arsenide present is Fe_5As.

Experimental Work

In the present research, the author used for methods in an attempt to determine the composition of the various phases: (1) chemical, (2) microscopic, (3) roentgenographic and (4) thermal.

Previous to this research, considerable time had been spent making analyses of different speisses, but unfortunately no very definite conclusions could be made as a result of these analyses.

Manuscript received at the office of the Institute April 30, 1934.

* Metallurgist, Harshaw Chemical Co., Cleveland, Ohio.

† References are at the end of the paper.

A study of the equilibrium diagrams involved was first made in the present work. The components of these diagrams might occur in the drosses and speisses and by synthesis; some characteristic might be found that would permit their identification in the various furnace products.

The System Fe-As

The iron-arsenic diagram was first studied. Only one of the three intermetallic compounds given in the diagram was successfully synthesized. The first attempts to synthesize the compounds failed because of the volatility of the arsenic. To obviate this difficulty, a new type of crucible was used. Four holes, each 0.5 in. in diameter and 3.5 in. deep, were drilled in a graphite rod, which was 2.75 in. in diameter and 4 in. long. This type of crucible was used only for making compounds and eutectic points; for melts containing lead a common fire-clay crucible with a borax cover was used.

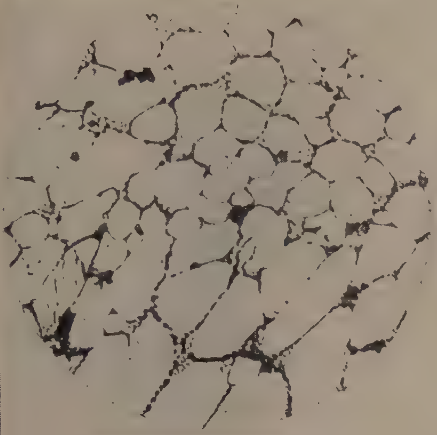
The finely powdered metals were carefully mixed and placed in the holes in the graphite rod and covered with borax glass. This improvised crucible was then placed in the furnace and heated at the top until the borax melted and formed a gastight cover. The crucible could then be heated rapidly without losing the volatile constituent.

TABLE 1.—*Metals Tested, with Analyses of Speisses*

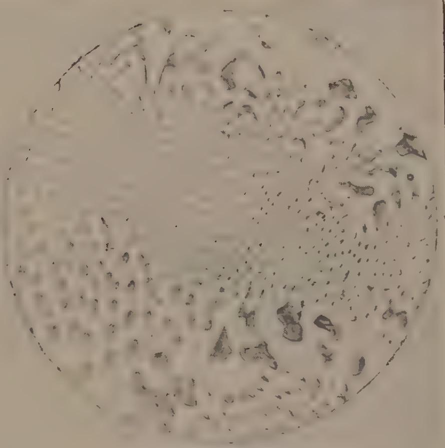
Test No.	Weight of Metals, Grams			Compound	Analyses of Speisses, Per Cent		
	Pb	As	Fe		Fe	As	Pb
1	200	20	15	FeAs	52.52	44.96	2.61
2	200	20	8	$FeAs_2$	49.27	48.20	2.42
3	200	20	30	Fe_2As	62.62	36.02	1.34
4	200	20	30	Fe_2As	64.08	34.50	1.42
5	200	15	35	Eutectic	71.55	28.20	0.24

Mixtures of the same composition were next melted with lead in order to determine the amount of lead retained by the different compounds occurring in the drosses. Table 1 gives the amount of metals used and the analyses of the speisses obtained from these fusions. These melts were cooled in the furnace. The crucibles were broken after removal from the furnace, in order to obtain the entire sample intact. Only the compound Fe_2As was formed in these melts, whether in the graphite rods or in the crucibles with lead. The other melts gave some of this compound, and sometimes some eutectic occurred, but no other compound could be identified. Fig. 1 illustrates the compound Fe_2As (No. 3 in Table 1). The principal constituent is Fe_2As with some Fe-As eutectic. The lead occurs as black spots around the grain boundaries.

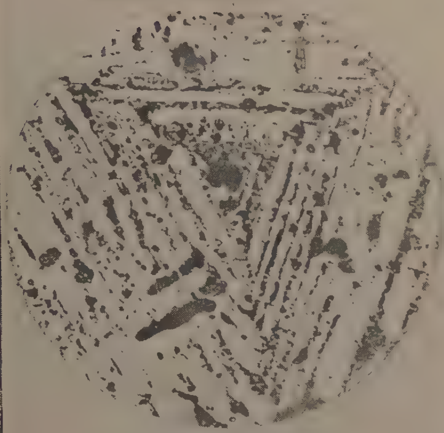
1



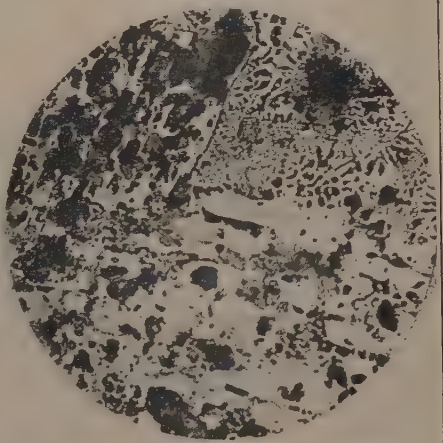
2



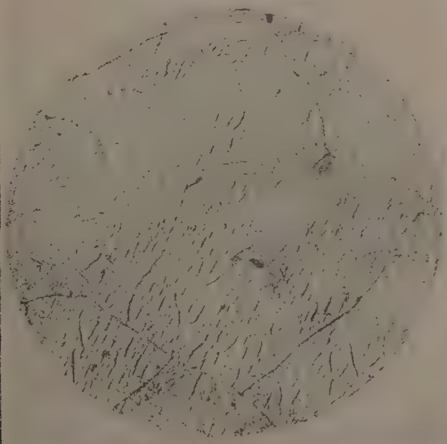
3



4



5



6

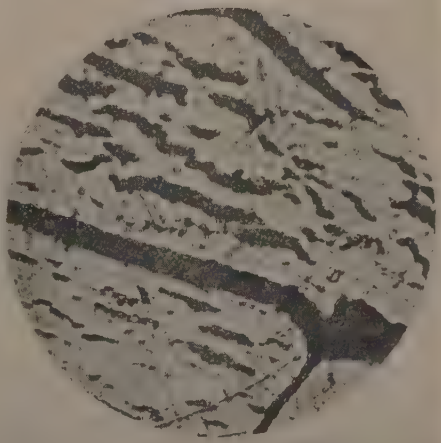


Fig. 1.—Fe_2As. × 100. Etchant, HNO_3.
Fig. 2.—Fe-As eutectic. × 100. Etchant, HNO_3.
Fig. 3.—Iron speiss, mostly Fe_2As. × 100. Etchant, HNO_3.
Fig. 4.—Iron speiss from plant No. 5. × 100. Etchant, HNO_3.
Fig. 5.—Cu_3As. × 100. Etchant, HNO_3.
Fig. 6.—Cu_3As and lead. × 600. Etchant, $FeCl_3$.

The common speiss from the blast furnace was examined. It consisted of crystalline plates of macroscopic size. An analysis showed the following composition: Fe, 60.53 per cent; As, 30.35; Cu, 4.20; Sb, 2.20; S, 2.10; Pb, 0.60.

The dross from plant 5 consists, to a large extent, of this platy arsenide and is illustrated in the photomicrographs.

Fig. 2 shows the Fe-As eutectic structure. The analysis is No. 5 in Table 1. Fig. 3 illustrates the common iron speiss as received. The light material is Fe_2As. Fig. 4 shows the iron arsenide from the dross of plant 5. The plates are Fe_2As, the eutectic of Fe_2As-Cu_3As, and black spots are composed of the eutectic of Cu_3As and lead with excess lead, as shown in Fig. 20.

The iron arsenides were next studied by X-ray methods. The space lattices were calculated from the diffraction patterns obtained on powdered samples. Wyckoff$^{(3)}$ gives the space lattice of Fe_2As as: $a = 3.62$ Å., and $c = 5.97$ A. This lattice is tetragonal and contains two molecules to the unit cell. The results obtained in this research, both on the synthetic melts and upon the samples from the different smelters, gave the following values: $a = 3.65$ Å., and $c = 5.99$ Å. A simple calculation shows two molecules to the unit cell:

$$\frac{(55.84 \times 2 + 75) \times (1.64 \times 10^{-24})}{(a^2 \times c)(10^{-8})^3} = 3.83$$

The figure obtained is approximately one-half the specific gravity found for the compound, hence there are two molecules in the cell. The diffraction pattern of the Fe-As eutectic gave lines of alpha iron, but no iron lines were found in any of the samples from the smelters. From these results it is concluded that the Fe-As eutectic is not present in the lead drosses, and that the only form is the compound Fe_2As.

Copper-arsenic System

The synthetic work was similar to that for the iron-arsenic system. It was found that only the compound Cu_3As formed, not only in the synthetic melts but also in the drosses and speisses from the smelters. This simplified the work considerably, since a superficial examination of the dross showed that the lead was mostly associated with the copper arsenide. The pure compound was made in the graphite crucible and also in fire-clay crucibles with lead. Table 2 contains the results of some of the fusions; it includes the series of lead-bearing Cu-As alloys from 20 to 90 per cent Cu. This series, Nos. 7 to 14 inclusive in Table 2, shows a peculiar lead-solubility curve having two minima, one at the eutectic point of Cu-As and the other at the compound Cu_3As. The lead retained by this compound is usually much higher. In fact, the author considers that it is only under ideal conditions of cooling that this low figure can be obtained. These melts were cooled slowly by leaving the crucibles in the covered furnace. It required about 12 hr. for the melts to reach room temperature. Regardless of the treatment, or of the ratio of copper to arsenic, only the compound Cu_3As formed. This is thought remarkable, since there are several Cu-As compounds found in nature.(4) The compound Cu_3As, known as Domeykite, Algodonite, Cu_6As, occurring in two forms, and Whitneyite, Cu_9As, which may occur in any of three forms.

The X-ray diffraction pattern, when calculated, gave the following values for the unit cell: a = 6.64 Å., c = 7.59 Å., c/a = 1.14. The cell is body-centered tetragonal and has six molecules in the unit cell as determined by specific gravity tests. The X-ray data give a value of 7.81 for the specific gravity while that determined of the sample was 7.9.

The diffraction patterns of the pure Cu_3As samples were identical with those obtained on the drosses from the smelters. This compound has a physical characteristic that allows it to be identified under the microscope; i.e., it is very brittle and invariably shows cracks. This is true also of the compounds Cu_3Sb and Cu_2S, but they are easily distinguished from the arsenide.

TABLE 2.—*Copper Arsenides*

Test No.	Weight of Materials Used, Grams			Products, Per Cent			Formula	Color, etc.
	Pb	Cu	As	Pb	Cu	As		
1	200	50	20	13.00	63.35	21.63	Cu_3As	Silvery, brittle.
2	200	100	20	11.33	74.71	13.83	Cu_6As	Fine grained, tough.
3	200	41	20	14.21	61.30	24.47	Cu_5As	Silvery, like No. 1
4	200	50	20	8.50	52.58	38.88	Cu_3As	Silvery, brittle.
5	200	100	20	5.42	66.86	27.51	Cu_6As	
6		71.8	28.2		69.75	30.25	Cu_3As	Very brittle.
7	200	20	80	56.71	19.70	23.56		Gray.
8	200	30	70	56.03	20.70	23.25		Gray.
9	200	40	60	53.90	24.84	21.22		Gray.
10	200	50	50	34.04	42.44	23.50		Lighter than 7–9.
11	200	60	40	6.62	67.52	25.82	Cu_3As	Fine grained, brittle.
12	200	70	30	19.62	55.48	24.83		
13	200	80	20	6.38	76.80	16.81		Eutectic.
14	200	90	10	20.10	73.28	6.63		Brassy, tough.

Fig 5 is a photograph of the pure compound, Cu_3As. Fig. 6 illustrates the compound when melted in lead. The sample was slowly cooled. Fig. 7 shows another sample of Cu_3As and lead. This contains one type of eutectic of Cu_3As and lead. The sample contains an excess of lead.

Fig. 8 contains the radial type of eutectic sometimes obtained. This sample was chilled rapidly from the freezing point.

It is pertinent to point out, at this time, that the speiss from the reverberatories that treat the dross is granulated by pouring into tanks of water. When this speiss is slowly cooled it is very tough and difficult to sample accurately. When quenched it is easily sampled. If the quenching temperature is around 1000° C., most of the lead is retained in solid solution. This phase will be discussed later.

Tests were made to determine the amount of lead held by the Cu-As alloys. Table 3 contains the results obtained.

TABLE 3.—*Copper Arsenides*

Test No.	Amount of Metal, Per Cent			Temperature, Deg. C.	
	Pb	Cu	As		
1	22.46	50.68	26.00	787	These samples were ladled out of the crucible and poured into a cold mold.
2	33.06	48.62	18.30	825	
3	32.82	48.97	18.30	880	
4	33.06	48.71	18.25	910	
5	33.06	48.75	18.15	1004	
6	15.10			886	(Cu and As added at 9:15.)
7	13.68			886	Sample taken at 10:30.
8	12.27			1025	Sample taken at 11:20.
9[a]	6.61	58.10		750	Melted and cooled slowly.
10	8.73	57.76			Cu_3As cooled slowly.
11	9.91	56.85			No. 10 remelted in Pb and cooled slowly.

[a] Composite of 6, 7 and 8.

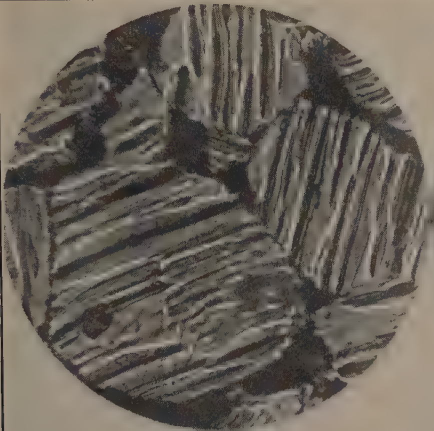
Nickel-arsenic System

Two compounds are given in the equilibrium diagram but only one was synthesized. The compound NiAs was obtained. This compound crystallized in thin plates similarly to the iron arsenide, Fe_2As. The plates were a reddish color. The system was not intensively investigated, as only one of the dross samples secured contained an appreciable amount of this element. The speiss from this plant gave a nickel arsenide similar to the one synthesized. It is assumed from these tests that only NiAs forms in the lead blast furnace.

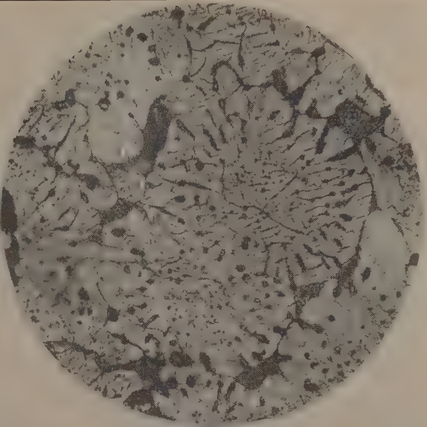
System Lead-arsenic

Percy(5) states that he secured compounds in this system, but later work has shown that no compounds occur. There is a liquid solubility and perhaps a slight solid solubility. It may be that the small percentage remaining in the lead after drossing is in solid solution. For example,

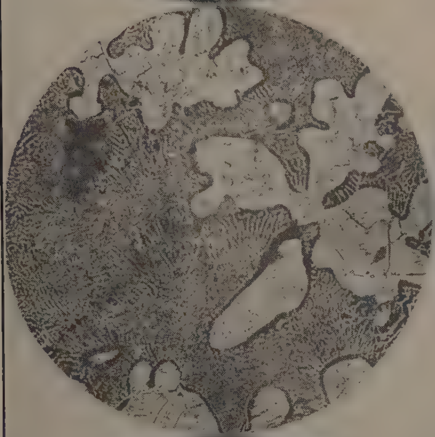
7



8

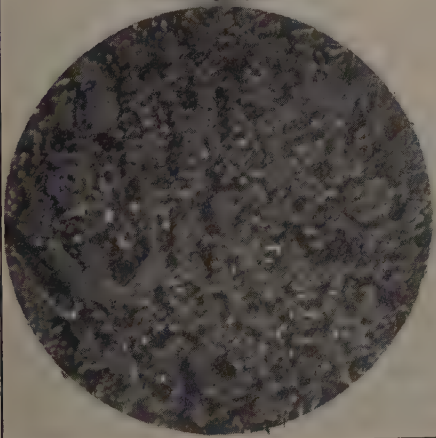


9



10

11



12

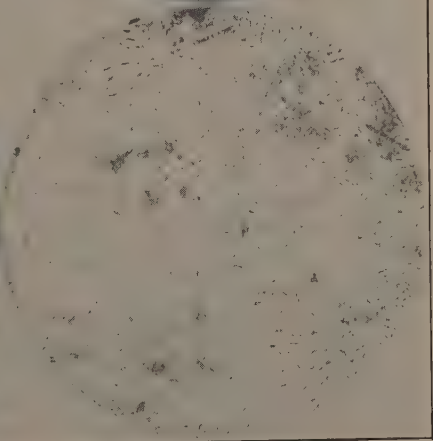


Fig. 7.—Cu_3As-Pb eutectic with Pb. × 600. Etchant, $FeCl_3$.
Fig. 8.—Cu_3As-Pb eutectic, radial type. × 400. Etchant, $FeCl_3$.
Fig. 9.—PbS-Cu_2S eutectic with excess Cu_2S. × 100. Etchant, HNO_3.
Fig. 10.—PbS-Cu_2S eutectic. × 100. Etchant, HNO_3.
Fig. 11.—Same as Fig. 10. × 1000. Etchant, HNO_3.
Fig. 12.—PbS-Cu_2S eutectic with excess PbS. × 100. Etchant, HNO_3.

at one smelter the copper and arsenic remaining in the lead after drossing were approximately 0.07 per cent each. The author believed that the copper was present as Cu_3As and the arsenic present as a solid solution; i.e., the arsenic above that required for the compound. This contention has not been proved.

System Iron-antimony

Two compounds are accredited to this system but only one was synthesized. The amount of lead retained by this compound averaged 1.5 per cent. This system is not considered important in the study of lead drosses and speisses, since the arsenide of iron will form in preference to the antimonide. If any smelter has drosses with a large percentage of antimony and but little arsenic, the iron antimonide should not cause a large lead loss, because it should approximate the above figure.

System Copper-antimony

Most of the drosses contain appreciable amounts of antimony as copper antimonide, and for this reason the system was investigated thoroughly. The entire system was treated as was the copper-arsenic system. Table 4 contains the results found in the alloys from 10 to 90 per cent Cu. The minimum point of the lead-solubility curve falls at the compound Cu_3Sb. Table 5 contains the results obtained in the attempts to determine the solubility of lead in this compound. The solubility figures are remarkably consistent. These figures, of course,

TABLE 4.—*Copper-antimony System*

Sample No.	Products Used, Grams			Analysis of Speiss, Per Cent			Color of Speiss
	Pb	Cu	Sb	Pb	Cu	Sb	
1	200	10	90	62.54	4.68	32.78	Silver gray, purple plates.[a]
2	200	20	80	60.28	9.73	29.93	As above.
3	200	30	70	60.08	14.90	25.00	No cleavage. Gray.
4	200	40	60	20.33	39.54	40.16	Purple.
5	200	50	50	11.34	44.78	43.81	Purple.
6	200	60	40	6.61	56.13	36.94	Silvery white.[b]
7	200	70	30	15.91	63.32	21.81	A stronger white.
8	200	80	20	19.62	63.51	16.95	Very light brass color.
9	200	90	10	30.73	62.55	6.74	More brassy than above.

[a] The Cu_2Sb crystallized in long blades. When the speiss was tapped it broke along these crystals of Cu_2Sb. This accounts for the purple color.

[b] The compound Cu_3Sb. This color is very distinctive but difficult to correctly describe, so that one not familiar with the color of the copper-antimony alloys could readily and accurately pick this particular alloy without the use of the microscope.

refer to the solubility just above the freezing point. There seems to be no increase in solubility at higher temperatures.

The equilibrium diagrams are not in agreement as to the compounds formed in this system; in some, Cu_2Sb, Cu_3Sb and Cu_5Sb_2 are given while in others only the first two are given. In the present work the first two were found, but even when samples were quenched from 1000° C. no evidence of the third, Cu_5Sb_2, was found. Although X-ray analysis allows only one-half molecule to the unit cell, sufficient proof was developed to convince the author that Cu_3Sb is a true intermetallic compound. This phase of the investigation will be discussed in another paper.

TABLE 5.—*Effect of Time on Solubility of Lead in* Cu_3Sb

Sample No.	Analysis of Speiss, Per Cent			Ratio Cu/Sb	Temperature, Deg. C.[a]	Time, Hr
	Pb	Cu	Sb			
1	6.73	57.45	35.91	1.599	1000	2[b]
2	6.56	57.13	36.28	1.574	1000	2[c]
3	6.62	57.22	36.15	1.583	1000	3
4	6.75	57.07	36.09	1.581	1000	4½
5	6.58	57.18	36.21	1.579	1000	5½
6	6.57	57.27	36.26	1.579	1200	6[d]

[a] Temperature at which a sample was ladled off the top, which contained a thick layer of Cu_3Sb.

[b] This sample was poured into an iron mold.

[c] Cooled in crucible.

[d] Cooled in furnace.

The antimony in the drosses and speisses from the smelters was present either as the compound Cu_3Sb or was contained in the metallic lead. The amount of antimony remaining in the lead after drossing often approaches 1 per cent.

System Nickel-antimony

The remarks made apropos the system iron-antimony apply equally as well here. It is considered that nickel will form an arsenide in preference to forming an antimonide. It is also considered that nickel, like iron, will react with copper arsenide to form an arsenide and metallic copper. Since the drosses studied contained more than the required amount of arsenic for the nickel, there is probably no nickel antimonide in the drosses and speisses.

System Lead-antimony

No compounds occur in this system. The antimony remaining after drossing is in solution until the freezing point is reached. The solid solubility is very low.

Complex Melts

Melts were made using all of the elements found in the drosses from the smelters. The compounds formed as in the simple melts and the predictions regarding the preferential formation of the arsenides held true. Iron arsenide, copper arsenide and copper antimonide were distinguished under the microscope. The lead sulphide was associated with the metallic lead. The presence of sulphides did not interfere in the formation of the other compounds. The synthesizing of these complex mixtures gave much information on the actual drosses and allowed interesting deductions to be made regarding the preferential formation of compounds.

Mattes

All of the drosses contained some sulphur and it was thought desirable to determine the constituents of the mattes. The synthetic melts contained only the sulphides of lead and copper. Cupric sulphide decomposes and forms cuprous sulphide at the melting point. Hence, all of the melts contained PbS and Cu_2S. The structures are illustrated. Fig. 9 is that of the PbS-Cu_2S eutectic with excess Cu_2S. Fig. 10 is that of the eutectic of the two sulphides, Fig. 11 that of the eutectic at high magnification, Fig. 12 that of the eutectic with excess PbS. The samples were all slowly cooled.

Reaction between Cu_3As and Fe

Scrap iron is usually added to the reverberatory furnace with the dross, which gives a better product than is obtained without its use. The copper speiss contains less lead, or, as it is expressed at the smelter, a better Cu-Pb ratio is obtained. It was found that only a small percentage was actually beneficial. At one plant it was the custom to use 6 per cent scrap iron. After a few tests it was found that less than 2 per cent was necessary. If the iron reacted with the copper arsenide and released the lead held in solution, it would be possible, at least theoretically, to secure a lead-free copper speiss. The iron reacts with the copper arsenide as indicated by this equation:

$$Cu_3As + 2Fe \rightarrow 3Cu + Fe_2As$$

This reaction goes to completion from left to right. The Fe_2As formed is easily distinguished under the microscope. Unfortunately, the metallic copper formed by this reaction forms an emulsion with the lead and the amount of lead that liquates out due to this reaction is very small. There is generally some lead sulphide in the dross, and at some plants it is added in small quantities to the reverberatory. Lead that liquates out from the addition of scrap iron is from the sulphide; the reaction:

$$PbS + Fe \rightarrow FeS + Pb$$

It is possible that the decomposition of PbS removes a dispersing agent, although the removal at this stage is not greatly beneficial, since the lead has already been dispersed, and the removal of the dispersant does not overcome its previous effects. The study of dispersing agents was not attempted. Manufacturers of metals containing Cu-Pb have used PbS, oil shales, and other reducing substances to effect a uniform dispersion of the lead in copper. Since the blast-furnace feed always contains PbS and other reducers, it is considered that some lead will be as the disperse phase in all copper drosses. FeS apparently does not disperse lead, otherwise the lead would not liquate from the above reaction. Table 6 contains the results found when scrap iron was added to copper arsenide containing 10.62 per cent lead.

TABLE 6.—*Results When Scrap Iron Was Added to Copper Arsenide*

Test No.	Metal, Grams		Analyses of Speisses, Per Cent			
	Cu_3As	Fe	Pb	Cu	As	Fe
1	60	3.0	8.73	61.60	26.90	2.80
2	49	4.9	8.73	61.90	23.80	5.60
3	50	10.0	8.73	61.65	21.20	8.40

The amount of lead in the speiss approximates that held when the speiss is cooled slowly. These tests indicate that the addition of iron to copper arsenide is not beneficial. Further tests were made by melting the dross from plant 4 and taking the speiss that contained 19.60 per cent lead with 6.50 per cent as lead sulphide, and treating it with iron. The iron first reacts with the PbS. The results are given in Table 7.

TABLE 7.—*Results of Treating with Iron*

Test No.	Metal, Grams		Fe	Speiss from Melts, Per Cent						
	Speiss No. 4	Fe		Pb	Pb as PbS	Cu	As	Sb	S	Fe
0				13.10	6.50	51.91	22.80	4.58	1.12	nil
1	106	6	5.35	16.40	nil	52.70	22.75	4.50	1.25	2.35
2	66	6	8.33	15.93	nil	50.55	22.30	4.45	1.20	5.58
3	70	8	10.2	15.34	nil	49.66	20.90	4.25	1.18	8.65
4	77	10	11.5	13.92	nil	49.22	20.40	4.10	1.15	11.16
5	108	25	18.8	12.04	nil	45.62	19.20	3.90	1.10	18.14

A sample of Cu_3As containing 16.40 per cent of lead was treated with varying amounts of iron. Three of the resulting speisses are given. Fig. 21 contains plates of Fe_2As in a background of Cu_3As and lead. The Fe_2As was formed by the following equation:

$$Cu_3As + 2Fe \rightarrow 3Cu + Fe_2As$$

The speiss contained 16.40 per cent lead and 2.35 per cent iron. Fig. 22 shows an increasing amount of Fe_2As. The speiss contained 15.34 per cent Pb and 8.65 per cent Fe. Fig. 23 shows a still greater amount of Fe_2As. The speiss contains 13.92 per cent Pb and 11.16 per cent Fe. The amount of lead released by this reaction does not appear to be economical.

Commercial Drosses

The commercial drosses were melted and the different products separated and analyzed. The percentages of speisses and mattes were calculated from weights. They varied from 20 to 90 per cent of the weight of the dross. The analyses of the drosses are given in Table 8. The dross numbers will be used consistently throughout. Table 9 contains the analyses of the speisses and mattes obtained when the drosses were melted in fire-clay crucibles.

TABLE 8.—*Analyses of Drosses*

Sample No.	Percentages						
	Pb	Cu	As	Sb	S	Fe	Ni
1	79.55	6.73	0.30	0.05	2.57	2.14	2.65
2	33.92	43.16	5.47	6.40	5.48	2.51	
3	79.79	10.38	0.60	1.00	2.15	1.12	
4	73.73	16.12	2.30	2.08	1.01	1.32	
5	81.08	8.89	2.13	0.45	0.20	1.10	
6	74.26	9.51	1.14	1.02	5.07	2.51	

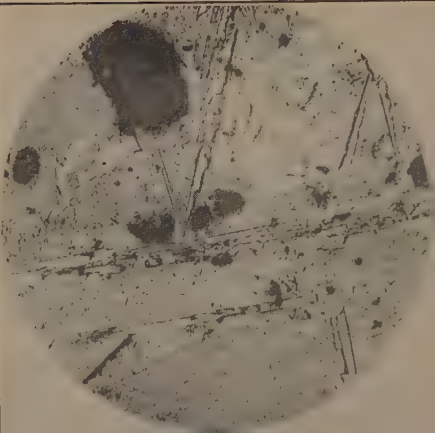
The analyses of the drosses are not complete, since only the elements given were determined. The drosses contain some silica, lime and minor amounts of other impurities.

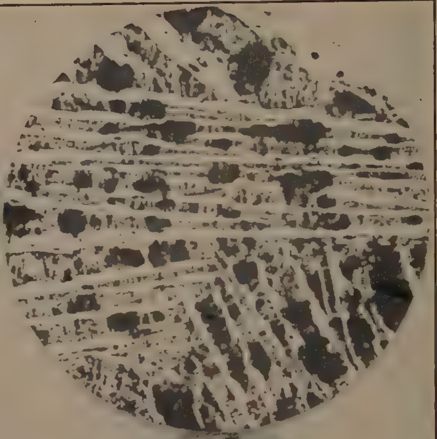
The photomicrographs show the structure of the nickel arsenide in the speiss from plant 1. Fig. 13 shows the rapidly cooled dross. The matte and speiss did not seperate well. The long crystals are NiAs, the dark areas contain the lead, the light background is Cu_3As and the darker background is Cu_2S. The matte-speiss from this melt was remelted and cooled slowly. Fig. 14 illustrates the nickel-copper speiss. The long crystals are NiAs; Cu_3As and lead are found between these crystals. No separation was effected between the NiAs and Cu_3As.

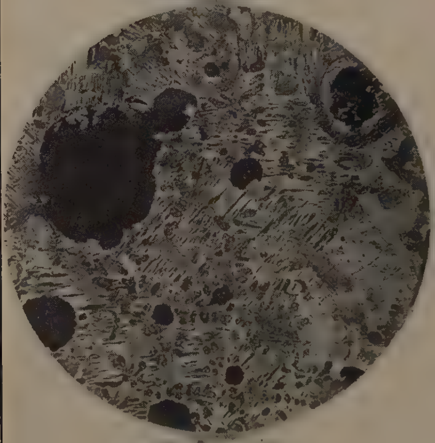
The lead is chiefly associated with the copper arsenide. It is hardly reasonable to expect to find a dispersing agent for the dispersion of a mixture of Cu_3As and lead in NiAs. The question then arises as to the reason for the failure of the two phases to separate when cooled slowly. The author uses the term "phase" to mean the mixture Cu_3As-Pb in this case. If the idea of a dispersing agent is discarded, an alternative theory presents itself. NiAs freezes at about 970° C. Cu_3As with lead was found to freeze at as low as 400° C. The difference in specific gravity is not great between the two compounds, hence there is no layering effect in the liquid state. This nonlayering, however, may be due to a solution tendency. As the liquid cools until the freezing point of NiAs is reached, plates of NiAs start forming. They are not all parallel but form at different angles. The intersections of these plates form pockets, which prevent the Cu_3As and lead from separating from the NiAs. One method of treatment would be to cool the solution to below the freezing point of NiAs but above that of the other constituents. The metallic lead could then be tapped off and some of the Cu_3As and lead will drain from NiAs. A similar condition exists in the copper-antimony series of alloys where Cu_2Sb occurs. With these alloys containing about 40 per cent lead, about one-half could be removed by this method. No photographs are given of the plates of Cu_2Sb but they

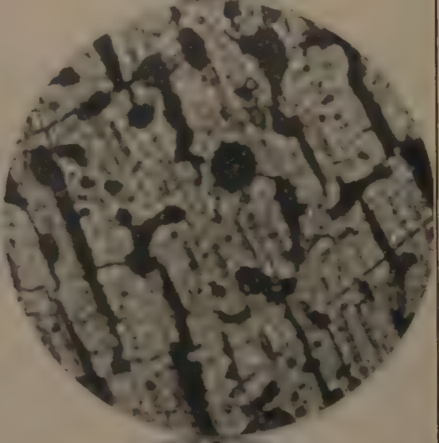
TABLE 9.—*Analyses of Speisses and Mattes When Drosses Were Melted in Fire Clay*

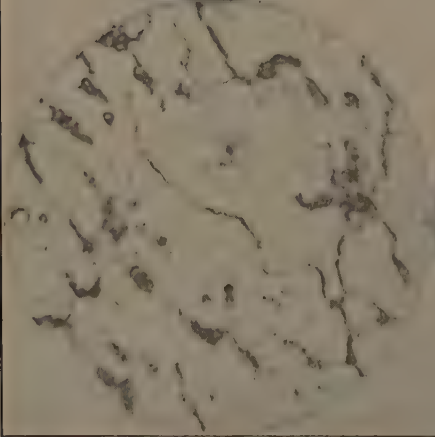
Sample No.	Percentages						
	Pb	Cu	As	Sb	S	Fe	Ni
1.							
Speiss	41.15	20.72	5.68	1.64	11.00	0.12	19.55
Matte	28.48	49.73	0.16	0.11	17.87	0.31	3.35
2.							
Speiss	24.97	54.36	9.58	8.35	2.48	0.21	
Matte	14.68	64.82	1.92	1.43	16.85	0.19	
3.							
Speiss	Insufficient quantity to analyze						
Matte	45.22	36.48	0.48	0.08	17.12	0.68	
4.							
Speiss	20.43	51.95	21.18	3.62	2.20	0.61	
Matte	27.38	49.97	2.64	1.94	17.42	0.57	
5.							
Speiss	1.18	24.78	28.16	0.89	2.45	42.48	
Matte	No matte separated						
6.							
Matte	51.42	30.15	0.54	0.33	17.43	0.18	
Speiss	Insufficient quantity to analyze.						

13


14


15


16


17


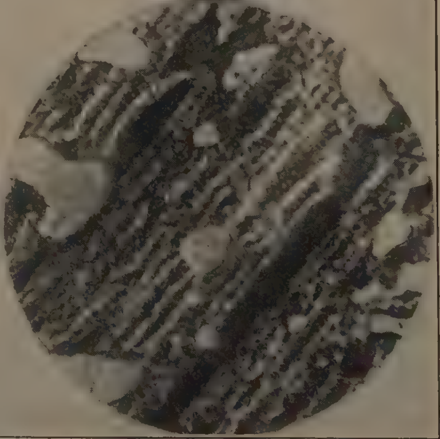
18


Fig. 13.—NiAs in speiss No. 1. × 100. Etchant, HNO_3.
Fig. 14.—No. 13 remelted. Cooled slowly. × 25. Etchant, $FeCl_3$.
Fig. 15.—Speiss No. 2. × 100. Etchant, $FeCl_3$.
Fig. 16.—Cu_3As and Pb. Speiss No. 4. × 600. Etchant, $FeCl_3$.
Fig. 17.—Fig. 16 quenched from 1000° C. × 2500. Etchant, $FeCl_3$.
Fig. 18.—Cu_3As-Pb eutectic. Speiss No. 4. × 1000. Etchant, $FeCl_3$.

form like the iron and nickel arsenides, freezing before the lead and holding it in the pockets formed by the intersecting plates. This condition exists only in the experimental melts, as the compound Cu_2Sb was never found in the furnace speisses.

Another method that may be beneficial for the nickel speiss would be to treat it with iron, which would react with the Cu_3As to form Fe_2As and Cu. If the NiAs-Fe_2As eutectic occurs near the NiAs end of the diagram the process should be economical. This eutectic may have a sufficiently low freezing point to permit working at low temperatures. If the Cu and Pb did not separate from this eutectic, PbS should be added. The reactions may be represented by the following equations:

$$Cu_3As + 2Fe \rightarrow 3Cu + Fe_2As$$

and

$$2Cu + PbS \rightarrow Cu_2S + Pb$$

This should give three products, metallic lead, iron-nickel speiss, and a matte consisting principally of copper sulphide. The reaction between copper and lead sulphide will not go to completion but will reach a state of equilibrium unless the lead is removed as formed. A double sulphide of lead and copper may form.

TABLE 10.—*Results of Treating Speiss with Iron and Matte*

Test No.	Speiss, Grams	Fe, Per Cent	Added Matte,[a] Per Cent	Speiss No. 2			Speiss	
				Matte, Grams	Lead, Grams	Wgt., Grams	Pb, Per Cent	Cu, Per Cent
1	400	2			20		25.50	50.0
2	400	4			28		25.05	50.8
3	400	6			32		25.96	50.0
4	400	8			80		23.60	50.0
5	400	10			0		25.13	49.8
6	400	15			0		25.96	48.0
7	400		10	78	24	324	32.33	44.8
8	400		15	112	38	266	30.68	46.0
9	400		20	130	53	275	32.10	46.4
10	400		25	140	70	262	28.32	48.8
11	400		30	165	90	242	38.23	40.8
12	400		50	255	154	167	25.05	46.8

[a] Matte from dross No. 3.

The speiss from plant 2 was very refractory. Table 10 contains the results obtained when this speiss was treated with iron and matte. The amount of lead recovered by the addition of these reagents varied greatly and is not consistent. The higher amounts of iron added gave no metallic lead. An increase in matte gave an increase in metallic lead liquated, a decrease in the amount of speiss, and a lower copper-lead ratio in the speiss.

Fig. 15 illustrates the complex structure of the speiss from plant 2. The sample was cooled rapidly. The dendritic forms are Cu_2S. The light material in the background is Cu_3As; the darker areas are composed of Cu_3Sb. The black spots contain the lead.

The speiss from plant 4 is a typical copper speiss. The copper-lead ratio in this speiss should remain fairly constant with a value of three. Table 11 gives the copper-lead ratios obtained when different elements and compounds were added to this speiss.

TABLE 11.—*Copper-lead Ratios*

	Material Added, Per Cent	Cu/Pb Ratio in Speiss
Arsenic	4.7	1.65
Arsenic	4.7	1.60
Antimony	7.8	1.00
Antimony	7.8	0.93
Arsenopyrite	4.0	
Scrap iron	5.0	1.78
Arsenopyrite	9.4	
Scrap iron	5.0	2.24
Antimony	4.0	
Scrap iron	5.0	1.15
Antimony	9.4	
Scrap iron	5.0	1.07
Copper	8.1	1.02
Copper	13.8	1.12
Scrap iron	3.2	3.13
Scrap iron	3.2	3.21
Scrap iron	3.2	2.82
Scrap iron	3.2	2.92

It has been shown that the function of the scrap iron is to reduce the lead sulphide present. This allows the lead originally present as the sulphide to liquate. Practically no lead is released by the reaction between copper arsenide and scrap iron. Some metallurgists claim that the addition of common iron speiss to the reverberatory charge is beneficial but it is shown herein that any beneficial action is due to increased fluidity and not to chemical action. The author does not believe that the use of this iron speiss is economical. Table 12 shows the amount of lead liquated from copper arsenide by the addition of common iron speiss. The sample of Cu_3As contained 12.98 per cent lead.

The photomicrographs of the speisses from plant 4 are conclusive as to the compounds that form. Fig. 16 shows the compound Cu_3As and lead. This sample is quite free from other constituents. It was cooled slowly. Fig. 17 is the same sample quenched from 1000° C. The lead remains in solid solution. Fig. 18 illustrates another sample from the same plant. This was cooled slowly. The eutectic of Cu_3As and lead forms the background. The light areas illustrate the solid solution of Cu_3As-Cu_3Sb. Fig. 19 illustrates the occurrence of sulphide inclusions. The surrounding mass is Cu_3As.

TABLE 12.—*Lead Liquated from Copper Arsenide by Addition of Iron Speiss*

Test No.	Cu_3As, Grams	Iron Speiss, Grams	Lead in Speiss, Per Cent
1	50	5	12.51
2	55	50	11.75
3	55	75	11.33

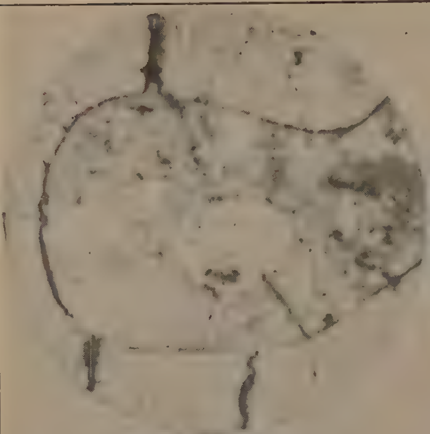
The different samples were used for securing the X-ray diffraction patterns. In all cases the compounds identified under the microscope were present. Sample 17 gave the lines of Cu_3As but the cell was larger because of the amount of lead in solid solution.

Only one illustration is submitted of the series in which iron speiss was added to the copper arsenide containing lead. The lead content was 12.98 per cent. Fig. 24 shows Fe_2As in Cu_3As. The speiss from this test contained 11.75 per cent lead. The amount of iron speiss added in this test was equal in weight to that of the copper arsenide.

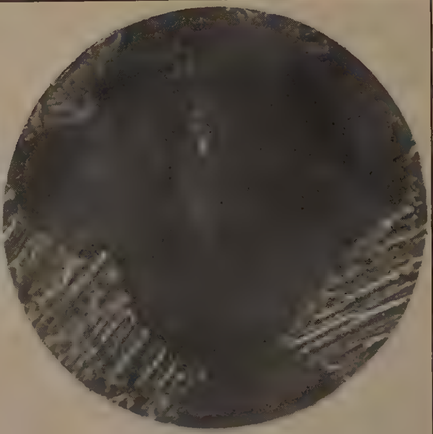
The speiss from plant 5 contains mostly Fe_2As. The lead in this speiss, as in the others, is found associated with the Cu_3As. Fig. 20 shows the Cu_3As-Pb eutectic with excess lead. This photograph was taken at the intersection of two plates of Fe_2As and illustrates the manner in which the plates prevent the separation of the lower freezing constituents. This photograph represents a spot on Fig. 4.

The drosses from plants 3 and 6 contained an insufficient amount of speiss-forming constituents to permit study, but it is assumed that the speisses from these plants would be comparable to that of plant No. 4.

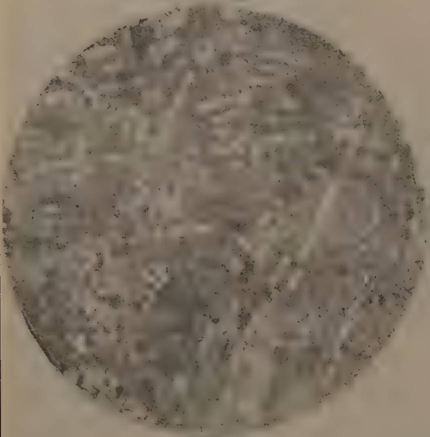
The photomicrographs of the mattes from the plants are not given. No. 1 contains the eutectic Cu_2S-PbS with excess Cu_2S, No. 2 contained the same constituents as the first, No. 3 is composed of the Cu_2S-PbS eutectic with excess PbS, No. 4 is the same as No. 1, No. 5 gave an insufficient quantity to examine, No. 6 contained an excess of PbS over the eutectic composition. Table 13 illustrates schematically the constituents of speiss formed in the lead blast furnace according to the author's work.



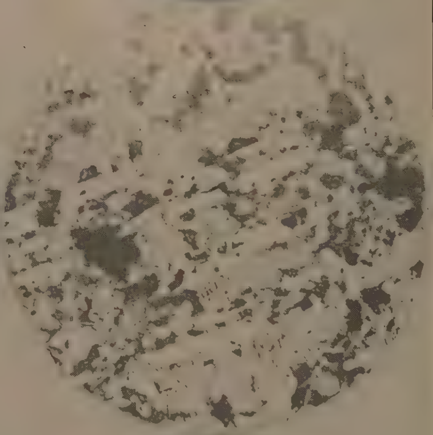
19



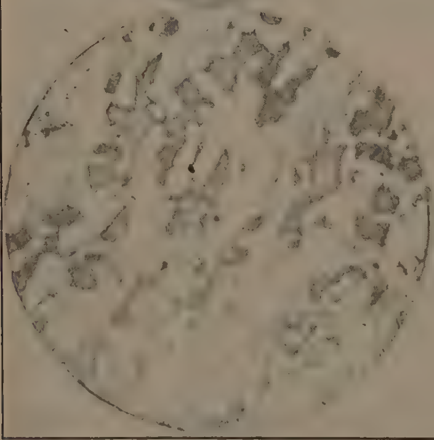
20



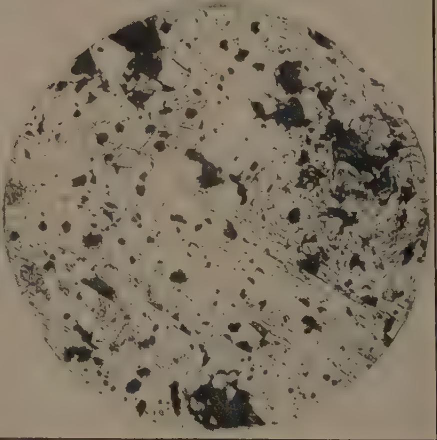
21



22



23



24

FIG. 19.—SULPHIDES IN Cu_3As. SPEISS NO. 4. × 3000. ETCHANT, $FeCl_3$.
FIG. 20.—Cu_3As-Pb EUTECTIC WITH Pb. SPEISS NO. 5. × 1000. ETCHANT, HNO_3.
FIG. 21.—Fe ADDED TO SPEISS NO. 4. × 100. ETCHANT, HNO_3.
FIG. 22.—FIG. 21 PLUS Fe. × 100. ETCHANT, HNO_3.
FIG. 23.—FIG. 22 PLUS Fe. × 100. ETCHANT, HNO_3.
FIG. 24.—SPEISS NO. 4. IRON SPEISS ADDED. × 100. ETCHANT, HNO_3.

CONCLUSION

This research proves the formation of the following intermetallic compounds in the lead blast furnace: Fe_2As, NiAs, Cu_3As, Cu_3Sb.

The first does not cause serious lead losses, the second is difficult to separate from Cu_3As, which causes the greatest loss of any of the compounds, and may be considered as a cause of lead losses; the third, of course, is the principal cause of lead losses, and the fourth is definitely bad.

One author(2) states that the common iron speiss consists of the compound Fe_5As. The evidence of chemical and röntgenographic analyses does not bear out this statement. The only compound found was Fe_2As. Another author(6) attempted to calculate the formula for the iron arsenide from chemical analyses. He obtained compounds having a high ratio of iron to arsenic, ranging from Fe_5As_2 to Fe_9As_2. Such calculations involve too many assumptions. This work has also shown that the arsenides formed in the blast furnace are not isomorphous. NiAs crystallizes in the hexagonal system, while Fe_2As and Cu_3As crystallize in the tetragonal system, the former is simple tetragonal and the latter is of the body-centered type.

TABLE 13.—*Constituents of Speiss Formed in Lead Blast Furnace*

Fe = Eutectic (may form)
+
As ↗Fe = Fe_2As
As →Ni = NiAs ↗+ As = Solid solution of As in NiAs
As →Ni = NiAs →+ Ni = Solid solution of Ni in NiAs
As →Ni = NiAs ↘+ Pb = Solid solution of Pb in NiAs (very doubtful)
As →Cu = Cu_3As ↗+ Pb = Cu_3As-Pb eutectic
As →Cu = Cu_3As ↘+ Pb = Solid solution of Pb in Cu_3As.
As ↘Pb = Solution of As in Pb (?) No compounds.

Sb ↗Fe = Does not form in presence of sufficient As
Sb →Ni = Does not form in presence of sufficient As
Sb →Cu = ↗Cu_3Sb + Pb. Solid solubility up to 6.6 per cent Pb (?)
Sb →Cu = ↘Cu_2Sb. Does not form in speiss (?)
Sb ↘Pb = Solid solution of Sb in Pb (?). No compounds.

The data in Table 2 indicate that pure Cu_3As need not contain more than 6.6 per cent lead. The lower figure at the eutectic point need not be considered, since the difference is not great and it is questionable whether the eutectic ever forms in the speiss. This figure was obtained by slow cooling.

The same percentage was found in the minimum point of the lead-solubility curve in the Cu-Sb series and fell at the compound Cu_3Sb. Table 4 contains the analyses of the speisses.

Since the complex speisses retain a much higher percentage of lead than the compounds alone, there must be other interfering factors, probably either the effect of dispersing agents or of an increased solubility. The additions of scrap iron, common iron speiss, or of lead sulphide do not decrease the lead loss appreciably. The author believes that it would be beneficial to tap off the liquid speiss from the reverberatory and pour into another small furnace. The addition of lead sulphide at this point should be more effective. The arsenic should volatilize as the sulphide, the copper should form a matte, and a large percentage of the lead should liquate.

The quenching of the speisses from the reverberatory furnace causes much of the lead to be retained in solid solution. A comparison of Figs. 16 and 17, the former cooled slowly and the latter quenched from a high temperature, gives an idea of the amount held in solid solution. It has been thought that lead is insoluble in the compounds occurring in the speisses but these photomicrographs indicate a solubility. The solid solubility at room temperature was not investigated.

ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to the American Smelting and Refining Co., the U.S. Smelting, Refining and Mining Co., and the Bunker Hill and Sullivan Smelter for the samples of drosses furnished for this research. Acknowledgments are due also to Prof. Albert Sauveur, Gordon-McKay Professor of Metallurgy at Harvard University, and to Dr. L. R. van Wert, Professor of Nonferrous Metallurgy at Harvard. Thanks are due to Dr. Carl E. Swartz and to Dr. S. J. Dickinson, of the American Smelting and Refining Co., for assistance in preparing the manuscript.

REFERENCES

1. C. Guillemain: Speisen und ihre zugutemachung. *Metallurgie* (1910) **7**, 595.
2. H. O. Hofman: Metallurgy of Lead, 355. New York, N. Y. McGraw-Hill Book Co.
3. R. W. G. Wyckoff: Structure of Crystals. New York, N. Y. Chemical Catalogue Co.
4. B. S. Butler and W. S. Burbank: The Copper Deposits of Michigan. U. S. Geol. Survey *Prof. Paper* 144.
5. J. Percy: Metallurgy of Lead. London. John Murray.
6. H. F. Collins: Metallurgy of Lead. London. C. Griffen and Co.

DISCUSSION

(*Carle R. Hayward presiding*)

G. L. OLDRIGHT,* Salt Lake City, Utah (written discussion).—Lack of space doubtless prevented the author from telling from his own experience and also from reviewing the literature as to how the described problems of lead drossing arose. The older practice of making matte-enrichment campaigns in the lead blast has been abandoned at many lead plants. Some of these plants send their mattes and speisses to copper plants, which return the lead, perhaps with the original or even some added arsenic, to the lead plant. In this way a circulating load of volatile impurities can be built up that both plants must handle.

---

* Supervising Engineer, U. S. Bureau of Mines.

C. A. Dice, T. B. Brighton and G. L. Oldright reached many of the same conclusions as Mr. Greene (see p. 127). The addition of iron scrap, for instance, was not found to free metallic lead when added beyond a certain quantity. Lead is soluble to considerable degree in FeS, as Leitgebel pointed out[7].

On fusing various quantities of copper with galena and allowing the mixtures to freeze into layers, it appeared from chemical and microscopical examinations that the reaction to form metallic lead was practically complete when the amount of copper added was only slightly in excess of the stoichiometric equivalent. Little metallic copper was found in the presence of PbS except when certain portions of FeS were present, when there might be some "moss copper" present, as pointed out by Tiedemann[8]. The temperature and time of fusion and the rate of cooling were found to have little effect on the amount of metallic lead retained.

The copper-arsenic system as worked on by Bengough and Hill[9] and the lead-arsenic system as shown by Heike were found useful[10]. There seems to be a series of solid solutions in the range of Cu-As composition from Cu_3As to Cu_5As_2.

By melting a series of copper-lead-arsenic alloys, and plotting on a triangular diagram, the areas were worked out by Messrs. Dice, Brighton and the writer where there is a one-layer and where there is a two-layer system showing immiscibility on cooling. In general, the area of immiscibility slopes toward the lead corner of the ternary diagram, there is less than some 25 per cent of arsenic present and from 95 per cent to almost no copper present.

The least amount of metallic lead (from 4 to 6 per cent) was retained when there was from 3.4 to 4.1 per cent of copper present for each per cent of arsenic when each mixture was allowed to settle until it froze.

As Mr. Greene stated, the copper-arsenic system retains far more lead then do the sulphide systems. There seems a good opportunity to separate both copper and arsenic from some smelter charges by improvements in the practice of flotation. In general, arsenic may be best roasted off in a reducing atmosphere before the charge is fused. Arsenic may be volatilized more quickly by using a roaster with hearths than by employing the Dwight-Lloyd sintering machine.

A. Zentner,* New York, N. Y.—Some years ago I had a striking illustration in treating zinc-plant residues in the reverberatory. Higher copper concentrates were being run than now, and we were treating them in the reverberatory and driving the zinc out as much as possible into the fuel. We had a coal running about 25 per cent ash, which caught fire rather slowly. We tried a different coal with a low ash, and there was a very marked difference in the temperature of the furnace at the burners. That end of the furnace was hotter, the smelting started sooner, we got a larger proportion of the furnace to the smelting temperature.

We later treated the residue in a blast furnace. One reason was that the copper then was lower, nevertheless it was higher than normally it would be in a lead smelter. As I recall it, our furnace charge ran about one per cent copper, and we found that the furnace froze up very rapidly because of speiss. The only way we could run at all was to increase the lead fall a great deal and run the furnace rapidly, and in that way get as high a temperature as possible in the crucible, and with the high lead fall, flush out or help to flush out some of the copper speiss. At that time, selective flotation had not done as good work as it does now, in producing high-lead concentrates, and the supply of lead concentrates was not enough to easily carry two smelters. These factors probably entered into the final decision to send the electrolytic-zinc plant residue from Great Falls to the East Helena lead smelter. They could bring up the lead fall, and, also, the copper content was reduced because of being added to much larger amounts of low-copper materials.

---

[7] *Metall und Erz* (1926) **23**, 439.

[8] Tiedemann: *Metall und Erz* (1926) **23**, 200.

[9] Bengough and Hill: *Jnl.* Inst. Metals (1910) **3**, 34.

[10] Heike: *Int. Ztsch. Metallog.*, **6**, 49.

* Consulting Engineer.

This paper brings back to mind the trouble we had because of the high copper content of the charges when smelting in a lead blast furnace. We solved the problem of treating the high-copper material, but the final economic answer was to send it to the East Helena smelter. Incidentally, this work was done in a copper blast furnace in which we cut the lead well opposite from the slag tap, so that the lead well and the slag tap were in the middle of the furnace on each side, and not with the slag tap at the end, like the usual lead blast furnaces. This was because the copper blast furnaces were there, and we simply changed one of them over to a lead furnace. The matter of the unorthodox position of the slag tap did not affect us.

O. P. CHISHOLM,* East Helena, Mont. (written discussion).—The author states that reverberatory smelting of dross is essentially a liquation process. The author is right in stating that analysis of different speisses resulted, unfortunately, in no very definite conclusions being drawn. However, for several years this writer has controlled dross reverberatory operations producing speiss from dross by being furnished with Pb, Cu, Fe, As, and S determinations. We have observed that with insufficient "collector," as in the case of speiss formation, the copper content and lead content were high. By the addition of some common speiss produced from the blast furnace, we have been enabled to produce a speiss with a higher ratio of copper to lead without lowering the copper content to a great extent. Economic reasons alone caused the accomplishing of the better ratio.

Before Mr. Greene's paper was published we had an idea that lead and arsenic formed a chemical compound and that a chemical reaction occurred when common speiss was added to the bath. Mr. Greene's experiments convince him that the Fe_2As only serves to form a fluid bath. Even if this is true, we have found its use very helpful at some of our plants for securing a speiss with improved copper to lead ratio. Its special use is for a case where the ratio of copper to arsenic in a speiss is high and the iron content is low. Usually a speiss of this type tapped hot from a furnace is very high in lead as well. We can definitely predict in such a case that the addition of Fe_2As improves the resulting speiss from the standpoint of higher copper to lead ratio. Of course, if too much common speiss is used, the percentage of copper becomes lower and the economic advantage may be lost. We have secured ratios of 7 Cu to 1 Pb by this procedure, but a lower than average copper content of the speiss resulted.

Mr. Greene's experiments show that metallic iron is of doubtful value in lowering the lead content of a speiss. In practice we have specific instances showing that the use of scrap iron will benefit copper to lead ratio. If the speiss has a high arsenic content and a low iron content, very often the lead percentage is high and the copper to lead ratio is low. An addition of scrap iron will improve the resultant speiss, for it probably forms Fe_2As, which in turn serves to form a fluid bath (to use Mr. Greene's explanation) and releases metallic lead. Were the arsenic content low enough, the addition of scrap iron would not be effective, for most of the iron would enter the slag.

We note an interesting point when comparing the speiss produced by Mr. Greene when melting dross sample No. 5 (see Table 8). The speiss is shown as No. 5 in Table 9. In actual practice this speiss tapped from the reverberatory, after perhaps a little doctoring with common speiss, would have about the following composition: Pb, 13.6 per cent; Cu, 42.4; Fe, 12.0; As, 24.0. These results seem to correspond more closely to the analysis as shown for dross sample 5 than the results secured by Mr. Greene in his fire-clay melt. He must have secured a neglible quantity of speiss to have 1.10 per cent Fe in the dross account for 42.48 per cent Fe in the resulting speiss. In actual experience about an 8 or 10 per cent "speiss fall" would result from melting the dross designated as No. 5.

---

* Lead Smelter Superintendent, American Smelting and Refining Co.

C. E. Swartz,* Cleveland, Ohio (written discussion).—In several places, Mr Greene mentions dispersing agents. It has been my contention that the difference in specific gravity and the pockets formed in the crystallizing of the higher melting speiss constituents have not prevented segregation of metallic lead in many speisses, but that this lack of segregation has been due to certain forces of adhesion between the metallic lead and the speiss proper. The nature of these forces is not entirely clear as yet. It may be a matter of surface tension or other force common to the colloidal dispersion. If so, these forces act on much larger particle sizes than is commonly supposed. Spheres of lead have often been observed in speisses that were at least ½ in. in diameter. It seems more probable that the lead is dispersed by some force such as secondary or residual valence. If this be the case, separation may be effected by satisfying these valences or by removing the negative radicals from the system. In other words, it is common knowledge that it is impossible to alloy copper and lead in anything like the concentrations that are found in speisses. Therefore the other constituents must be the stabilizers or dispersing agents. These constituents are arsenic and antimony and to lesser extent sulphur. If these constituents are completely removed, the two metals should readily separate, and, conversely, if enough of these constituents were added to satisfy the copper and lead completely separation should take place as all secondary valence or forces of adhesion would be satisfied. It is well known that in spite of the great affinity of copper and arsenic to form compounds, when arsenic is present in insufficient quantity to satisfy the copper present, some arsenic will be found dissolved in the lead. The copper is then trying to combine with this arsenic and the lead is trying to retain it in solution and at the same time reject all but a small amount of the copper present, thus we have a good chance for an emulsion to be formed.

In trying to liquate lead from speiss by repeated heating and cooling, it has often been observed that there is a small button of hard lead after each operation. Another point that is less often observed in such experiments is the arsenic vapors that leave the melt. If the theory of dispersing agents being responsible for occlusion of lead by speiss is correct, these two observations of lead separating out and arsenic vapor coming off are closely related.

On p. 176, Mr. Greene states that at 1000° C. most of the lead is retained in solid solution. I have examined a number of quenched speisses and compared them with the same speiss slowly cooled. A rough measure of the lead areas has always indicated the same degree of separation in both.

G. U. Greene.—My work was completed prior to Mr. Oldright's and his colleagues, but I did not get the material written up until after the completion of his work.

Dr. Swartz's comments are more from a theoretical standpoint and while I also have given evidence to the effect of dispersing agents, I do not place them in the same order as does Dr. Swartz. Furthermore, I do not exactly approve of this term of residual valence. However, I feel that this is a subject which is not sufficiently clear to apply to this study as yet. As to his criticism of my finding the solid solubility of lead in copper arsenide, I can only reply that I only reported what I found.

Results of different investigators in a study of this kind vary mostly because of different materials and varying physical conditions.

---

* The Cleveland Graphite Bronze Co.

Softening of Lead Bullion

By Arthur E. Hall,* Member A.I.M.E.

The operation of "softening" in lead refining is designed, as the word implies, to separate from the bulk of the lead the elements that tend to make lead hard. These elements, which invariably are present in argentiferous lead, interfere with the desilverization, and must be almost entirely absent in refined desilverized lead. They are mainly copper, antimony, arsenic and tin.

The properties utilized in accomplishing this separation are the low solubility of copper or copper sulphide in lead at its freezing-point temperature, and the greater and selective affinity for oxygen of the other elements at temperatures of the order of 700° to 900° C., or, in the presence of sufficient alkali, at a temperature of about 500° C.

The major problems of softening lead bullion lie in the necessary subsequent treatment of the by-products of the primary operation, which contain, either chemically or mechanically, lead or reagents that must be isolated for market or re-use. Therefore an important objective of the primary operation must be the highest practicable concentration of these elements in the by-products.

Within the past three decades, during which the writer has been engaged in lead refining, the technique of softening lead bullion has had as many variations as there were lead refineries. This was the result of the variation in composition and character of lead bullion received.

The writer has received for refining shipments of lead bullion varying as widely as indicated by the following table:

Sb, Per Cent	As, Per Cent	Sn, Per Cent	Cu, Per Cent	Ag, Oz. per Ton
1.00	0.05	nil	0.05	70
0.50	2.50	2.00	0.50	200
3.50	0.50	nil	0.30	350

At times these have been received uniformly and at other times irregularly with a variation from week to week as wide as those shown. Under such conditions, establishment of a universal softening technique presented many problems. Such variations existed because refinery tolls too often were based on a ton of bullion, whatever its composition, and

---

Manuscript received at the office of the Institute, Aug. 6, 1936.

* Consulting Metallurgical Engineer, Carlsbad, New Mexico.

there was a lack of coordination between the concentration mill (if one were involved), the smelting plant and the lead refinery.

Because of distribution requirements and transportation costs, much lead bullion has been shipped from lead smelter to lead refinery in the shape of cold bars. These would vary from bars liquated at the smelter and containing only about 0.05 per cent copper, to those having a top crust of copper dross, due to hot molding, and containing, averaged over the combined weights, frequently more than 0.5 per cent copper. Shipments of cold bars have been received so high in arsenic that the bars would break if not carefully handled. Such material approaches a composition which should be termed speiss rather than bullion.

In general, in the order of selective affinity for oxygen, the elements stand as follows, although reversible reactions often alter the relations: (1) arsenic, (2) tin, (3) antimony. However, this selectivity is not sharp enough to avoid economically the production of oxidized by-products grading from high to low content of an individual element.

The refiner has been obliged not only to separate lead from the elements named, but also to market antimony and tin, which requires a rather clean-cut separation between antimony and tin and the separation of these elements from the lead or reagent involved in the by-products containing them. The fusibility of any softening by-product is greatly decreased by the presence of tin oxide, and this has been another source of embarrassment.

The presence of large percentages of arsenic in lead bullion at times has been due to the desire to produce arsenious acid at the smelter and the resultant crowding of the lead blast-furnace charge with arsenical material; a major portion of this arsenic was collected in high concentration by the fume-filtering apparatus serving the blast furnace, but the arsenic content of the lead bullion was nevertheless increased above normal. Such bullion resulted in very low concentrations of arsenic plus antimony in softening by-products, by any procedure, theoretically indicated by:

Sb_2O_3 . . . 1 lb. oxygen required by 5 lb. antimony.
As_2O_5 . . . 1 lb. oxygen required by 1.875 lb. arsenic.

$$2Sb_2O_3 + 3As_2O_3 = 4Sb + 3As_2O_5$$

Such undesirable metallurgical conditions have been greatly lessened in North America, Australia and England, and most of the lead bullion being softened today by a refinery contains insignificant amounts of tin and a high ratio of antimony to arsenic. This improvement in metallurgy can be ascribed to:

1. The refining of large amounts of bullion at the smelter—Trail, Kellogg, Port Pirie, Monterrey, Midvale and Peñoles—and greater understanding and coordination between smelter and refinery, so that bullion

is treated for copper either at the smelter or at the refinery before being charged to the softening operation.

2. Employment of selective flotation, which has generally purified lead blast-furnace charges.

3. Preparation of blast-furnace charges by sintering, which more evenly distributes the reduction reaction through the charge. This helps the softening because it tends to divert more arsenic to fume-filtering apparatus and less to lead bullion.

These salutary measures (from the refiner's standpoint) do not prevent the purchase by the smelter of profitable (even if complex) ores or the concentrates therefrom, and tend to a better over-all metallurgy.

In view of the facts just stated, a fairly comprehensive discussion of lead softening involves much less complexity today than it would have 10 or 20 years ago.

General Procedure

Elimination of Copper.—Elimination of copper is effected by:

1. Cooling lead bullion with agitation to a temperature closely approaching freezing point, in a kettle, which gives a dross high in copper and a residual bullion containing about 0.05 per cent copper;

2. Introducing crushed sulphur into the residual bullion in a way to give intimate contact, thereby reducing the copper content of the bullion to about 0.005 per cent.

Elimination of Antimony, Arsenic, Tin.—Several methods are used for elimination of these impurities, as follows:

3. Lead bullion containing 0.005 to 0.05 per cent copper is charged to a softening furnace in which its temperature is raised to between 700° and 800° C. Oxidation of impurities is stimulated by agitation and by addition of lead oxide (litharge and other oxidized by-products from various refinery operations, high in lead oxide). The temperature of the residual metal is reduced to about 500° C. and the metal is transferred to the succeeding desilverizing operation.

4. The ratio Sb-As-Sn to lead in slags so formed in the softening furnace is materially increased by addition of alkali salts to lead oxide by-products charged to the softening furnace as oxidizer.

5. Molten decopperized lead bullion is continuously sprayed by means of a centrifugal pump through a bath of molten alkali salts (preferably NaOH plus NaCl) until softened, at a temperature of about 470° C., with a uniform and continuous addition of sodium nitrate or some oxidizer like lead oxide.

6. Continuous softening, actually today commercially applied to reverberatory-furnace softening and suggested for procedure No. 5, is a procedure in which molten decopperized bullion runs into one end of one or more units in a continuous flow and leaves at a corresponding rate

after having been subjected to one of the treatments indicated in procedures 3, 4 or 5.

Discussion of Methods

Elimination of Copper

1. Hot lead bullion from the blast furnace, from which large infusible chunks of speiss-matte, if present, have been removed, is agitated in a kettle until cool. The agitation is accomplished by stirring machines, or submerged water or air pipes. The material is cooled to a temperature closely approaching the freezing point of the metal. The copper dross in rising entrains much metal. It is stirred briskly for 30 to 40 minutes with small additions of ammonium chloride, coal, rosin, sugar, sawdust or some similar material, and thus is freed from entrained metal and becomes a fine black powder. This powder contains about 10 per cent copper and the residual metal contains about 0.05 per cent copper.

2. This having been accomplished, and the bullion being at the lowest possible fluid temperature, finely comminuted sulphur is introduced into intimate contact with the lead; for example, by a controlled flow of sulphur into the vortex produced by a stirring machine. More dross, entraining much lead, arises. This is continued until about 1½ lb. sulphur per ton of lead has been introduced. The dross is then stirred as in procedure No. 1. The final dross removed will contain more than 10 per cent copper and the residual metal will contain about 0.005 per cent copper. This process is covered by United States Patents No. 1386503 (Hulst, 1921), No. 1706722 (York, 1929), No. 1891978 (Gross, 1932).

Further treatment, at least in lead refineries far from copper-converting plants, depends upon treatment schedules offered by such converting plants for copper products and may be:

a. The black powder is smelted in a reverberatory furnace with a small amount of lime-silica flux at a temperature of about 1000° C., producing: (1) speiss-matte, 60 per cent copper for shipment; (2) leady slag, returned to blast furnace; (3) metal, returned to copper elimination.

b. The black powder is smelted in a reverberatory furnace with galena at moderate temperature, producing an arsenic-free matte about 20 per cent copper. To this 20 per cent matte is added scrap iron, which precipitates lead and produces a matte containing more than 40 per cent copper, for shipment.

From the standpoint of softening lead bullion, the desirability of removing copper at this stage lies in the avoidance of a closed circuit of copper. If not so eliminated the copper is ultimately returned to the softening furnace in litharges used as oxidizers. Closed circuits of impurities have been the most common causes of high refinery costs.

Elimination of Other Impurities

3. Lead bullion, having been decopperized to a point between 0.005 and 0.05 per cent copper, is received in a reverberatory furnace, by gravity or pump or as cold bars. Its temperature is raised to about 700° C. and a controlled amount of lead oxide (litharge, fumes, etc., from other operations) is introduced. The bath is agitated at such a temperature that an equilibrium is approached, possibly 35 per cent antimony in the slag and 0.2 to 0.5 per cent antimony in the metal, representing a condition where the slag is fluid and free from silver. This slag is removed. The residual metal is further agitated and subjected to further calculated additions of lead oxide, until the antimony content of the metal is reduced to less than 0.01 per cent. The furnace and contents are then cooled to about 500° C. and the metal is transferred to desilverization kettles by gravity. Chilled slag, comparatively high in lead oxide and low in antimony oxide, remains in the furnace in frozen condition awaiting a succeeding charge. The slag removed from the furnace is reduced to antimonial lead, generally in a silver-free blast furnace. This process is covered by United States Patents No. 1285714 (Hulst, 1918) and 1950387–8–9 (Betterton, 1934). It has been described by Maier and Hincke[1].

High arsenic and/or tin ratio to antimony seriously interferes with this procedure. While increasing antimony oxide materially lowers the melting-point temperature of a mixture of the oxides in a slag within the range involved, tin oxide has the opposite effect and tends towards entrainment of metal and consequent silver in the slag, which necessitates an intermediate partial reduction of the slag to recover the silver. As indicated by molecular composition, both tin and arsenic decrease the possible concentration of antimony in softening slags and greatly diminish the possible total antimony plus tin plus arsenic concentration therein.

Antimonial lead produced from slags containing considerable arsenic and tin requires treatment for elimination of these elements to render it marketable.

It may be treated by the Harris process for the selective separation of arsenic and tin; or if it contains 14 per cent antimony, 2 per cent tin, 2 per cent arsenic, it may be stirred at 400° C. and will yield a metal low in tin (0.05 per cent) and a powdery dross containing about 14 per cent antimony, 10 per cent tin, 2 per cent arsenic. Lead so treated is then stirred with caustic soda (about 2 lb. caustic soda per pound of arsenic) which will reduce the arsenic content of the metal to about 0.05 per cent and give a slag containing lead and possibly 10 to 20 per cent arsenic oxide.

---

[1] *Trans.* A.I.M.E. (1932) **102**, 97.

There are methods still in vogue in which no attempt is made to produce essentially silver-free slags from the softening furnace, thus necessitating an intermediate "partial reduction smelting of slags to desilverize" before reduction to antimonial lead. This causes an abnormal run-around of impurities and precious metals, which, however many reasons there may be for it, is bad metallurgical practice and deserves consideration only to the extent of discussion as to means of avoiding it. Such a discussion can be constructive only if carried on in the light of lead metallurgy as a whole.

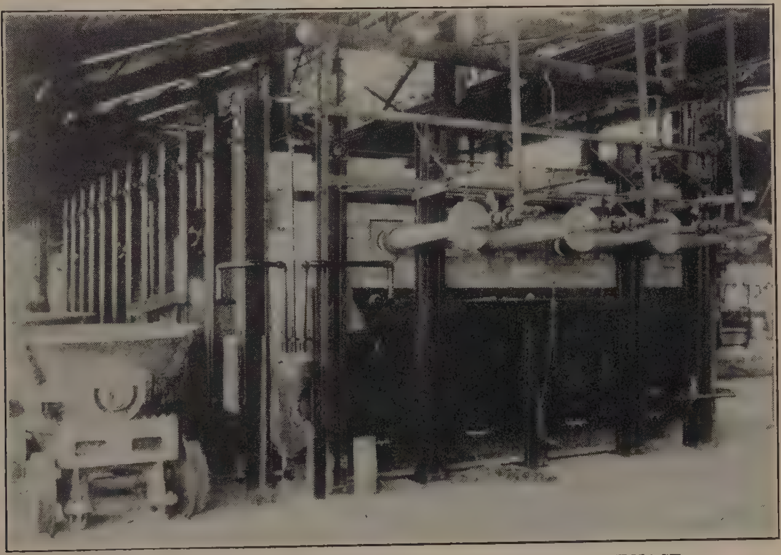


FIG. 1.—TYPICAL REVERBERATORY SOFTENING FURNACE.

A typical reverberatory softening furnace is illustrated by Fig. 1. The elevation of the furnace is established so that the furnace will discharge its contents by gravity through a taphole into the kettles of the succeeding operation. Fig. 2 shows in the foreground a launder in place through which 200 tons of softened lead bullion has been discharged into a kettle. Longitudinal concrete piers and transverse steel beams (which can be seen just above the working floor in Fig. 1) carry a rectangular, welded steel-plate jacket, the sides and ends of which are double and form a water jacket. The discharging cooling water pipes are shown in the foreground.

Fig. 3 illustrates a typical refractory lining. Modern furnaces have thicker side walls than are shown here and use special refractories at the slag line but the top and bottom arches are generally of good quality firebrick. Tapholes are provided at both the level of the inverted arch in the middle of the furnace and at the sides of the furnace. Some furnaces are built with tapholes at the end, the bottom of the furnace sloping towards them, which makes possible a complete discharge of the furnace contents. This is not to be recommended when slag should be left in the furnace to react with the succeeding charge, nor when cold bars are charged into a softening furnace. The first furnace described is designed to leave 50 to 100 tons of bullion in the furnace to protect the

Fig. 2.—Kettles with a launder in place, through which 200 tons of softened lead bullion has been discharged.

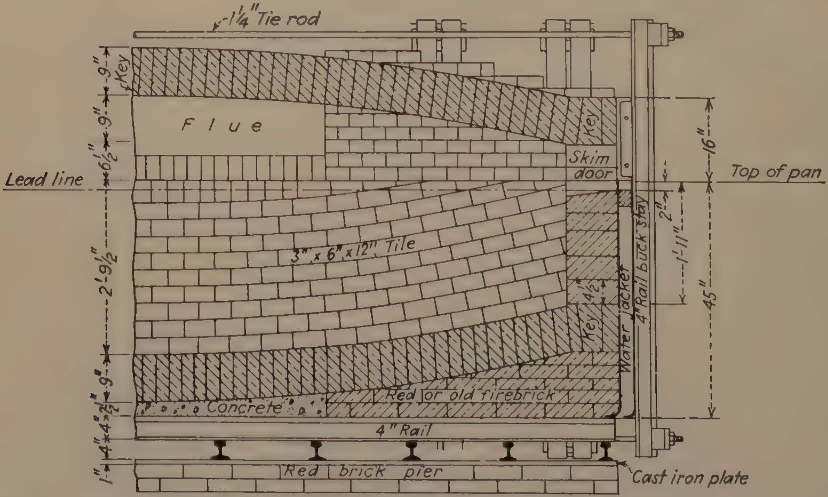


Fig. 3.—Transverse section of softener, showing typical refractory lining.

bottom from corrosion and shattering. With such protection, bottoms frequently have a life of 15 years.

The furnace shown in Fig. 1 has a hearth area of 12 by 27 ft. and delivers 200 tons of softened bullion through a taphole at the top of the spring of the inverted arch. It will eliminate 4000 to 5000 lb. of antimony in a 24-hr. cycle, depending upon the initial antimony content. The furnace has a damper in the flue, and often has an auxiliary burner in the side wall, to insure proper temperature all over the hearth area.

Volatilization of lead in this operation does not exceed 3 lb. per ton of bullion treated. Volatilization of antimony is something less than 10 per cent with bullion containing 1 to 2 per cent antimony.

The consumption of fuel is approximately 750,000 to 1,000,000 B.t.u. per ton of bullion containing 1 per cent antimony.

4. One remarkable phenomenon, which has been the basis of hundreds of patents and processes, is the quantitative sharpness of selectivity in the affinity of oxygen for lead and antimony plus arsenic plus tin, in the presence of sufficient alkali salt. An example of this, which is cited only to indicate possibilities, is an experience of the writer some 16 years ago.

A most unusual sulphide concentrate was the subject of experimentation in the laboratory and small furnace. Its composition was about as follows: lead, 40 per cent; zinc, 20; antimony, 10; tin, 5; arsenic, 1; silica, 2; iron, 1 per cent; silver, 200 oz. per ton. This, roasted and smelted in conventional manner, yielded a very hard bullion. If dead roasted and melted with just sufficient sodium carbonate to supply soda for the production of sodium zincate, antimonate, stannate, arsenate, silicate, and ferrate, and just sufficient reducer to correspond to the lead content, the fusion resulted in the production of a nearly pure lead containing quantitatively all of the silver and a slag quantitatively free from silver and lead. Every attempt to reduce the amount of soda from the proportion stated resulted in silver and lead in the slag.

This experiment illustrates the basic principle of the use of alkali salts in lead refining.

It is possible, therefore, in a softening furnace to increase materially the ratio Sb-As-Sn to lead in slags from that furnace by the addition of alkali salts, incidentally decreasing the melting temperature of such slags (particularly when tin is present) and making possible the reduction from such slags in whole or in part either complete or selective. Such practice is of economical advantage when slags containing soda are available from other operations.

5. A cast-iron cylindrical receptacle several feet in diameter and deeper than the depth of molten lead bullion to be treated, with an outlet at the bottom fitted with a valve controlled from above, is sunk in a kettle of molten lead bullion to a depth approaching the total depth of bullion, insuring a seal of lead, and is charged with a molten mixture of caustic

soda and common salt. A vertically driven centrifugal pump submerged at the bottom of the lead bullion bath, outside of this cylinder, continuously pumps a stream of lead bullion through the alkali and out at the lower end of the cylinder to the main bath of bullion, without entrainment of alkali.

For example, in a kettle 14 ft. in diameter and 7 ft. deep, a cylinder 6 ft. in diameter may be used with a 3 to 4-ft. depth of alkali. Into this alkaline bath is pumped molten lead bullion at a rate of 30 tons, or 85 cu. ft., per minute. Also, at a rate proportioned to the rate of oxidation required, cold sodium nitrate or lead oxide is fed into the cylinder by means of a mechanical feeder.

With such an apparatus, 500 lb. of antimony-arsenic-tin has been converted into antimonate, arsenate and stannate of sodium per hour, and the operation continued so that the bullion is freed from antimony, arsenic and tin at a temperature of 480° C. with no volatilization of lead or of the several impurities involved. With proper manipulation, no lead is left in the alkaline salts.

The cylinder can be supported by motor-operated trunnions, by means of which it can be tipped far enough to decant the alkaline product into a launder in which flows a hot, weak solution of caustic soda and sodium chloride resulting from a subsequent operation.

The practical requirements of reagents for successful separation are:

Reagents, Lb.	For 1000 Lb. Sb	For 1000 Lb. As	For 1000 Lb. Sn
$NaOH$	1500	2900	1912
$NaCl$	354	819	524
$NaNO_3$	620	1000	520

In the separation of antimony, arsenic and tin from one another, several properties of the various alkaline salts are utilized:

Sodium antimonate is insoluble in water or alkaline solution and more readily filtered from a solution containing common salt, which is in this case an electrolyte.

Sodium arsenate is much more soluble in hot and/or concentrated solution of caustic soda than in cold and/or weak solutions of caustic soda.

Sodium stannate, very soluble in water, is quite insoluble in strong (1.4 sp. gr.) solutions of caustic soda.

Sodium stannate in weak alkaline solution, if heated with calcium carbonate, will yield a precipitate of tin and calcium rather free from arsenic (if present).

Sodium arsenate crystallized by cooling from an alkaline solution invariably carries with it a certain proportion of tin (if present).

Insoluble sodium antimonate from alkaline solution invariably contains a constant percentage (about 2 per cent) of tin (if present).

Alkaline solutions of sodium arsenate can be causticized by treatment with milk of lime, yielding insoluble calcium arsenate and a 10 per cent solution of caustic soda.

These properties are cited to show that procedures of treating the alkaline by-products must vary as the proportion of the impurities varies, just as in furnace softening.

Therefore, only one example is given of the treatment of alkaline salts from this process—a treatment that was applied to many thousands of tons of lead bullion:

The alkaline salts were dissolved in the available weak (10 per cent NaOH) solutions to a specific gravity of 1.4. Antimony and tin salts are insoluble, and when filtered the cake contained some arsenic. The strongly alkaline filtrate was chilled and the sodium arsenate crystallized therefrom was filtered out. The filtrate was transferred to a triple-effect evaporator for the recovery of anhydrous and molten caustic soda for re-use. The sodium arsenate was dissolved in water and causticized with milk of lime, yielding insoluble calcium arsenate, which was wasted, and a 10 per cent caustic soda solution, which in part was used for the solution of primary alkaline salts and in part transferred to the evaporator.

The antimony-tin cake from the first filter was treated with water, yielding a sodium stannate solution and a sodium antimonate filter cake. The cake was dried and reduced to metallic antimony. The solution was purified of lead, tellurium, etc., by boiling with shot tin and was again filtered and electrolyzed hot, with iron insoluble anodes, in iron-lined tanks, for the production of pure tin. The spent electrolyte was transferred to coolers, where arsenic was crystallized therefrom. The liquor was transferred to evaporators for the recovery of molten caustic soda for primary operation.

6. A recent development of continuous lead refining, by G. K. Williams (U. S. Patent 2043524) deserves the utmost consideration. That process is described by Mr. Williams in this volume (p. 226).

Conclusion

The remarkable developments in selective flotation in recent years, in combination with improvements in preparation of the charge and in operation of lead blast furnaces, mean that today over-all economical lead metallurgy probably does not involve sending large proportions of arsenic and tin to a lead refinery in lead bullion; these impurities can much better be separated from the lead at the mill or the smelter than after lead bullion has been produced. This might be interpreted as an effort to shift responsibility from one branch of the service to another. But when all is said the objective is to produce lead as cheaply as possible and separations should be made where they can be made with the least expense, irrespective of artificial and complicated transfer schedules, often designed to take advantage of abnormal conditions.

The capital expense involved in a lead refinery can be multiplied several times if an effort is made to design a refinery that will take care of "anything."

Debismuthizing Lead with Alkaline Earth Metals, Including Magnesium, and with Antimony

By Jesse O. Betterton* and Yurii E. Lebedeff†

As a matter of the most widespread interest to lead-refining metallurgists, the process of desilverizing lead originated by Parkes is the most fundamental step in lead refining. While this basic operation, in addition to effecting a practically complete recovery of gold and silver, is also a great purifying operation and a governor on the purity and uniformity of the final refined lead, it has the important deficiency that no bismuth is removed in the operation. The problem of finding a satisfactory, inexpensive method for removal of bismuth that would fit in with the basic desilverization step has been one of enticing interest for lead-refinery metallurgists for many years. Of late it has become one of imperative interest, and while many attempts and much progress have been made, it is probably fair to say that metallurgical progress thus far is only catching up with commercial requirements.

The Pattinson process, an original competitor of the Parkes process for desilverization, has received much attention for its possibilities for bismuth removal. Bismuth concentrations in the Pattinson process fall far short of the silver concentrations and as a result too many operations are required and a crawl in grade in the kettle units is experienced which requires periodic correction. Altogether, it has proved too expensive a remedy, from the cost standpoint of both installation and operation.

The Betts electrolytic process is a fully satisfactory remedy but its present status in the field of lead refining is more a matter of bismuth removal than preference as a refining system, except, of course, in instances particularly favorable to the basic requirements of the process. The Betts process, of course, is essentially different from the Parkes process, and very difficult to associate therewith to any economy except in minor ways. Accordingly, where economy dictates the Parkes process, and this is true of far the greater portion of the world's tonnage, the adoption of the Betts process primarily for bismuth removal is apt to prove an expensive remedy on account of its normally higher cost of operation, inelasticity of the equipment for variable tonnages, and high per ton cost of installation.

Manuscript received at the office of the Institute July 28, 1936.

* General Manager of Lead Refineries and Director of Research, American Smelting and Refining Co., Maurer, N. J.

† Research Metallurgist, American Smelting and Refining Co., Maurer, N. J.

From the foregoing it will be evident that conditions were favorable for the reception and development of Dr. Wilhelm Kroll's pioneer work with the alkaline earth metals. Dr. Kroll first indicated to metallurgists that such a separation could be made and his basic patent* gave sufficient data from laboratory experimentation to make it appear worth while to try for a commercial development of the idea.

The early history of this development in the American Smelting and Refining Co. was attended by many difficulties and disappointments. Even though the attempt was comprehensive and extended over a period of about two years, involving laboratory experimentation, small-scale development, and, finally, rather extensive tests in full-sized lead-refining kettles, the results were far from satisfactory. It appeared that too much calcium reagent was required, that the operation itself was slow and required particular skill, that the final lead could not be entirely freed of calcium, and finally, that the cost of the process would materially exceed any commercial allowance that could be made for it. Accordingly the data were collected and reviewed, and the project was discontinued.

However, as the demands for some such process were on the increase, the matter was revived by the authors of this paper, with the thought that a thorough study of the basic characteristics of the process by means of closely controlled experimentation directed thereto might result in sufficient metallurgical improvement to place the process on a commercial basis.

In the description of this development, we will follow more or less the sequence of events that led to the present status of the process and established it as both a metallurgical and commercial success in the field of lead refining, as evidenced by its use in the current, commercial treatment of comparatively large tonnages of lead. Accordingly this will be given under four main headings, as follows: (1) debismuthizing with calcium, (2) debismuthizing with magnesium, (3) debismuthizing with calcium and magnesium, (4) debismuthizing to very low limits with antimony.

I. Debismuthizing with Calcium

The principles governing the removal of bismuth from lead with calcium are very similar to those regulating the removal of silver from lead with zinc, the reagent instead of zinc being calcium, preferably a calcium-lead alloy containing 3 to 3.5 per cent calcium. The active reagent is Pb_3Ca, as will be noted from the constitutional diagram of the Pb-Ca series in Fig. 1.

---

* U. S. Patent No. 1428041. Subsequent Letters Patent of the United States, owned by the American Smelting and Refining Co., are Nos. 1853534, 1853535, 1853536, 1853537, 1853538, 1853539, 1853540, 1853541, 1979442, 1989734 and 2032788.

The procedure followed in both cases consists essentially of three major steps: (1) proper incorporation of the reagent both in respect to time of stirring and temperature of metal bath; (2) removal of the dross containing the compound or compounds of the reagent and the impurity to be removed, which rises to the surface of the metal bath because of its lower specific gravity; and (3) cooling of the metal bath to practically the freezing temperature, with further removal of the drosses formed on cooling.

In our first attempt to develop a commercial process we made three important mistakes; namely, the use of too much reagent, the addition of the reagent at too high a temperature, and the incorporation of the reagent into the bath with too long a mixing period. Fig. 1 indicates that in cooling from too high a temperature the excess reagent will freeze out as Pb-Ca liquations, adding materially to the weight of the dross formed and the difficulty of separating it from the bath. The use of excess reagent is not only a prohibitive expense from the standpoint of reagent cost but it also greatly complicates the operating procedure. The tests in Table 1 have been selected from our experimental data to show the extent of bismuth removal by variable calcium additions, and to illustrate the ineffectiveness of excess calcium additions. In all experiments the final lead was tapped from beneath frozen crusts of excessive weights.

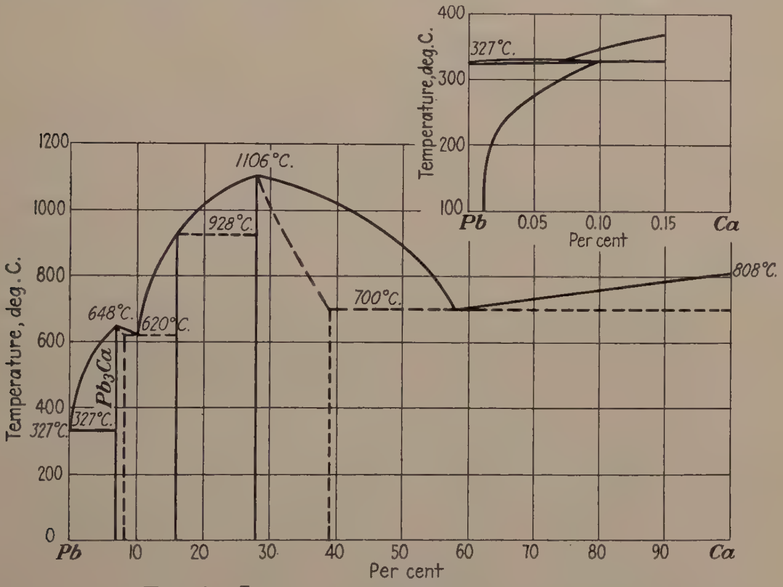


FIG. 1.—LEAD-CALCIUM EQUILIBRIUM DIAGRAM.

Table 2 is included to show the effect of various calcium additions within the range of commercial work, particularly the low side of reagent

TABLE 1.—*Removal of Bismuth by Calcium**[a]

Bismuth in Original Metal, Per Cent	Calcium Addition, Lb. per Ton	Percentage of Original Metal, by Weight, Frozen as Crust	Analysis Metal Withdrawn from under Crust, Per Cent	
			Bi	Ca
0.140	3.0	37.3	0.048	0.069
0.140	2.0	30.1	0.058	0.057
0.140	1.5	21.7	0.071	0.040
0.140	1.0	23.6	0.090	0.029
0.140	0.5	19.3	0.128	0.017
0.045	8.0	41.4	0.030	0.071
0.045	3.0	34.5	0.040	0.070

[a] Two hundred pounds of lead was used in each test. Calcium-lead alloy containing 5.05 per cent calcium and 0.015 per cent bismuth was used. The alloy was added at 690° F., bath mixed 10 min. at that temperature and then allowed to cool to freezing. At the freezing temperature the molten metal was withdrawn from under the frozen crust through a special spout and spigot attached to the bottom of the kettle.

additions and following a practical operating procedure of removing the drosses by skimming. It is also an illustration of the experimental methods used in approaching and determining the minimum reagent additions.

TABLE 2.—*Effect of Calcium in Commercial Work*[a]

Bismuth in Original Metal, Per Cent	Calcium Addition, Lb. per Ton	Percentage Original Metal Removed as Dross and Rim on Cooling to Freezing	Final Metal Analysis, Per Cent		Calcium Distribution, Per Cent of Addition	
			Bi	Ca	To Metal	To Crust
0.163	2.0	10.1	0.060	0.059	53.1	46.9
0.163	1.5	8.6	0.083	0.044	54.5	45.5
0.163	1.0	9.2	0.114	0.030	55.0	45.0
0.163	0.5	10.8	0.155	0.019	68.2	31.8

[a] Two hundred pounds of lead was used in each test. Calcium-lead alloy containing 5.05 per cent calcium and 0.015 per cent bismuth was used. The alloy was added at 660° F., metal bath mixed 10 min. at that temperature and then allowed to cool to freezing. The drosses formed on the surface of the metal bath after mixing the alloy and upon cooling to freezing, and the solidified rim on the inside circumference of the kettle were removed. The metal bath was then reheated, the kettle sides well scraped, and this dross also removed. The metal was then carefully sampled and the analytical results obtained are indicated in the above tabulation under the heading "Final Metal Analysis."

The temperature of the bath at the time of reagent incorporation is a factor of great importance. Bismuth-calcium liquations will not freeze out from ordinary low-grade bismuth lead at moderate working temperatures, as Table 3 will illustrate. A practical effect of this is to add more reagent at higher temperatures than is necessary or desirable in order to balance the apparent lack of debismuthizing. Final separation of the dross is impeded by too much reagent and the net result is a waste of free reagent into the dross, more oxidation of reagent, and a false determination of the amount of reagent actually required.

---

* In all tests tabulated in this paper refined lead of approximately the following composition was used: Silver, 0.0005 per cent; copper, 0.0004; zinc, 0.0005; iron, 0.0002; antimony, 0.0005; arsenic, 0.0000; bismuth as indicated.

TABLE 3.—*Effect of Temperature of Bath*[a]

(Calcium addition at 800° F. equivalent to 2 lb. per ton)

	Percentage of Original Metal Removed as Dross	Analysis of Metal, Per Cent		Calculated Analysis Dross Removed, Per Cent		Calcium Distribution, Per Cent of Addition	
		Bi	Ca	Bi	Ca	To Metal	To Dross
Original bath		0.163					
Dross skimmed at 800° F.	3.5			0.12	0.43		15.0
Bath at 800° F. after skimming dross		0.163	0.085			85.0	
Dross skimmed from 800° to 750° F.	1.5			0.163	0.16		3.0
Bath at 750° F. after skimming dross		0.163	0.084			82.0	
Dross skimmed from 750° to 700° F.	1.6			1.137	0.38		6.0
Bath at 700° F. after skimming dross		0.143	0.079			76.0	
Dross skimmed from 700° to 650° F.	2.3			2.59	0.69		16.8
Bath at 650° F. after skimming dross		0.082	0.063			59.2	
Cooling dross and rim removed from 650° F. to freezing	8.7			0.28	0.13		11.2
Bath after cooling dross removed		0.060	0.056			48.0	

[a] Calcium-lead alloy containing 3.21 per cent calcium and 0.10 per cent bismuth was used in the above test. The alloy was added to the metal bath at 800° F. and mixed one minute at that temperature. One hundred and seventy pounds of lead was used for this test.

Too long stirring in incorporating the reagent adds to the loss of reagent through oxidation, particularly at higher temperatures. The weight of dross is likewise greatly increased, an effect apparently of incipient oxidation of the calcium.

In view of the foregoing, it will be clear that the best procedure is one that tends to minimum calcium additions at minimum temperatures, and with the least stirring consistent with proper incorporation of the calcium into the bath.

Table 4 shows the effect of the addition of calcium in stages. Likewise, it brings out the important conclusion that the Bi-Ca compound actually present in the dross removed has the formula Ca_3Bi_2. Because of the strongly exothermic reaction between bismuth and calcium, it has been found impracticable to make up the Bi-Ca constitutional diagram, although some very thorough attempts have been made. This is due to

TABLE 4.—*Effect of Addition of Calcium in Stages*

	Weight, Lb.	Analysis of Metal, Per Cent		Ca-Pb Alloy Addition			Dross Removed, Calculated Analysis, Per Cent	
		Bi	Ca	Lb. Ca per Ton	Analysis, Per Cent		Bi	Ca
					Ca	Bi		
Original bath	204.5	0.900						
First calcium-lead addition[a]	4.69			1.03	2.29	0.37		
First dross removed	2.7						9.1	2.4
Bath after first dross removed	206.5	0.781	0.020					
Second calcium-lead addition	4.0			0.91	2.29	0.37		
Second dross removed	16.0						2.6	0.6
Bath after second dross removed	194.5	0.621	0.021					
Third calcium-lead addition	4.94			1.11	2.29	0.37		
Third dross removed	13.5						3.1	0.7
Bath after third dross removed	186.0	0.434	0.030					
Fourth calcium-lead addition	4.75			1.04	2.29	0.37		
Fourth dross removed	14.10						2.6	0.7
Bath after fourth dross removed	176.7	0.259	0.037					
Fifth calcium-lead addition	4.13			0.92	2.29	0.37		
Fifth dross removed	8.75						2.8	0.8
Bath after fifth dross removed	172.0	0.134	0.053					
Sixth calcium-lead addition	4.31			0.96	2.29	0.37		
Sixth dross removed	4.30						1.9	0.6
Bath after sixth dross removed	172.0	0.096	0.096					
Cooling dross and rim removed	50.0						0.18	0.12
Bath after cooling dross removed	122.0	0.059	0.086					

[a] Each addition of calcium-lead alloy of analysis indicated above was mixed 2 min. at 650° F., after allowing 5 min. for melting, previous to mixing. The drosses formed after each addition of alloy were removed at 650° F. Calculation of the drosses is given in Table 5.

the destruction of the laboratory apparatus by the high temperatures resulting. Most of the curve has been explored and the compound Ca_3Bi_2 arrived at in all the experimental efforts. Table 5, therefore, is a confirmation reached by a totally different method.

Table 5.—*Calculation of Calcium-bismuth Compound Ratio in Drosses Formed and Removed at* 650° *F. in Test Indicated in Table* 4

	Total Contents, Lb.		Calculated Contents of Metal Mechanically Held in Dross, Lb.		Compound Contents by Difference, Lb.	
	Bi	Ca	Bi	Ca	Bi	Ca
First dross	0.246	0.066	0.020	0.0004	0.226	0.066
Second dross	0.420	0.095	0.096	0.0030	0.324	0.092
Third dross	0.417	0.100	0.057	0.0040	0.360	0.096
Fourth dross	0.367	0.100	0.037	0.0050	0.330	0.095
Fifth dross	0.243	0.068	0.012	0.0050	0.231	0.063
Sixth dross	0.081	0.025	0.004	0.0040	0.077	0.021
Total	1.774	0.454	0.226	0.0214	1.548	0.0433

$$\text{Ratio of Bi to Ca in compound} = \frac{1.548}{0.433} = 3.57$$

$$\text{Ratio of Bi to Ca in } Ca_3Bi_2 = \frac{416.0}{120.2} = 3.46$$

Table 6 is a reagent table based on our experience for various grades of bismuth-bearing lead to produce lead with a final content of about 0.048 per cent bismuth.

Table 6.—*Calcium Required to Produce Final Lead of* 0.048 *Per Cent Bismuth Content*[a]

Bismuth Content Original Lead, Per Cent	Calcium Requirement, Lb. per Ton of Lead Treated	Bismuth Content Original Lead, Per Cent	Calcium Requirement, Lb. per Ton of Lead Treated
0.10	2.0	0.60	5.0
0.20	3.0	0.70	5.5
0.30	3.5	0.80	6.0
0.40	4.0	0.90	6.5
0.50	4.5	1.00	7.0

[a] This table is applicable only to lead containing less than 0.01 per cent combined arsenic plus antimony.

Effect of Impurities

Based on our experience, arsenic or antimony in excess of 0.01 per cent will be removed by calcium before any appreciable elimination of bismuth occurs. It is important, therefore, that these impurities be within this limit for the most economical and successful operation. Our results indicate the formation of compounds Ca_3Sb_2 and Ca_3As_2.

Zinc below 0.3 per cent does not combine with calcium when debismuthizing lead containing, for example, 0.2 per cent bismuth. If the zinc is in excess of 0.3 per cent, our results show that about one pound of calcium is consumed in removing 5.5 lb. of zinc at temperatures above 660° F. Below this temperature the ratio is about one pound of calcium to 11 lb. of zinc, indicating a different and a higher zinc compound.

There is no indication of copper removal when desilverized lead containing 0.001 per cent copper or less is debismuthized with calcium.

Silver in desilverized lead is very slightly removed, but to no practical extent, by the addition of calcium.

II. DEBISMUTHIZING WITH MAGNESIUM

Paralleling debismuthizing with calcium, we have used magnesium alone. With the ordinary grades of bismuth-bearing lead bullions encountered at the refineries, and with anything like economical additions of magnesium, no debismuthizing takes place. This is clearly demonstrated by results of tests shown in Table 7.

TABLE 7.—*Removal of Bismuth with Magnesium*[a]

Original Bismuth Content, Per Cent	Magnesium Addition per Ton Lead Treated, Lb.	Percentage of Original Metal, by Weight, Frozen as Crust	Analysis Metal Removed from under Frozen Crust, Per Cent	
			Bi	Mg
0.180	8.0	38.2	0.188	0.380
0.180	3.0	34.6	0.185	0.146
0.180	1.0	22.5	0.180	0.048
0.60	20.0	33.7	0.15	0.991
0.60	10.0	33.4	0.40	0.498
0.60	3.0	30.2	0.58	0.146
0.60	1.0	21.6	0.60	0.046
0.93	10.0	30.8	0.52	0.461

[a] Magnesium added to a lead bath of 200 lb. in the form of magnesium turnings. The addition was made at 660° F. to the vortex of a mixer. Total mixing time varied from 5 to 10 min. at 660° F., depending upon the amount of magnesium used. After the incorporation of magnesium, the metal bath was allowed to cool to the freezing temperature and the molten mother liquor was withdrawn from under the frozen crust through a spout and spigot arrangement attached to the bottom of the kettle.

Debismuthizing becomes apparent on bullions of about 0.5 per cent bismuth for moderate use of reagent, but even for this grade anything like effective bismuth elimination would require a prohibitive amount of magnesium. This is apparent from the tests in the second and third sections of Table 7.

Owing to the fact, however, that the bismuth problem is often dealt with at smelting plants by segregated smelting, thus producing a small amount of high-bismuth bullion, in order to clean the greater portion of the bullion, the use of magnesium alone for debismuthizing at the refineries becomes of considerable interest.

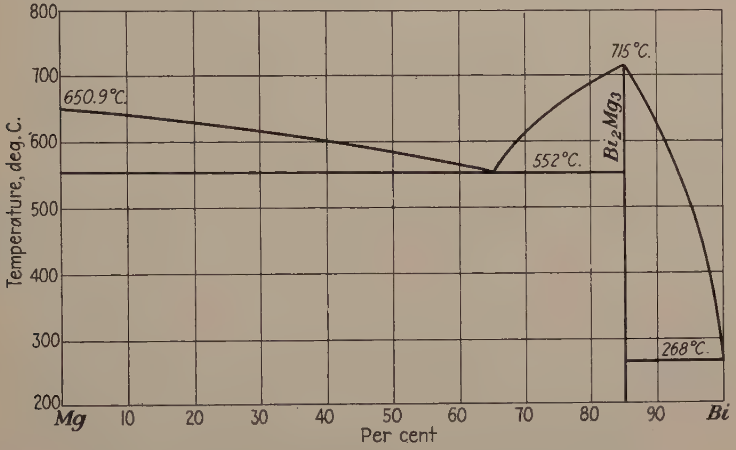


Fig. 2.—Bismuth-magnesium equilibrium diagram.

Table 8 illustrates an application of magnesium alone for the removal of bismuth from lead containing high percentages of bismuth. The procedure followed in this test is similar to that used in plant operations, except that in practice metallic magnesium is used instead of lead-magnesium alloy. The solution of magnesium metal is easily accomplished by submerging the cast magnesium pigs in a perforated iron basket, under the surface of the lead bath, and then impinging a stream of lead, issuing from a pump, directly on the magnesium held in the basket. Calculations in Table 9 show that the bismuth is removed by magnesium in accord with the formation of a definite compound Mg_3Bi_2.

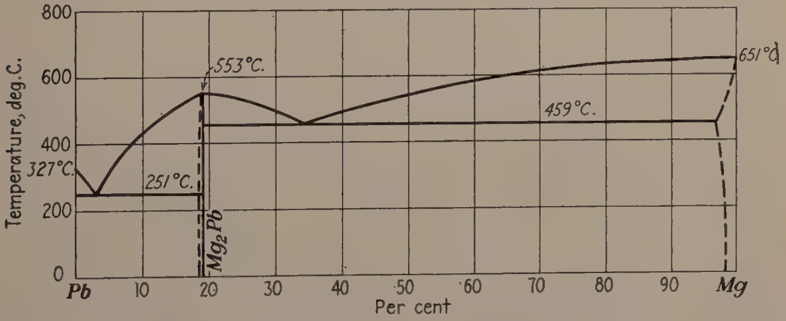


Fig. 3.—Lead-magnesium equilibrium diagram.

TABLE 8.—*Effect of Magnesium on Lead Containing High Percentages of Bismuth*[a]

	Weight, Lb.	Analysis of Metal, Per Cent		Dross Removed, Calculated Analysis, Per Cent	
		Bi	Mg	Bi	Mg
Original bath	171.2	4.12			
First addition of magnesium-lead alloy	6.29	0.2	12.40		
First dross pressed and removed at 660° F.	8.0			24.4	4.08
Bath after first dross removed at 660° F.	169.4	3.02	0.268		
Second addition of magnesium-lead alloy	5.35	0.2	12.40		
Second dross pressed and removed at 660° F.	10.4			25.1	4.34
Bath after second dross removed	164.3	1.52	0.402		
Dross and rim removed in cooling to freezing	55.0			2.98	0.65
Final bath	109.3	0.78	0.277		

[a] Magnesium was added to the lead bath in the form of a magnesium-lead alloy containing 12.40 per cent magnesium and 0.2 per cent bismuth. The first addition was made at 730° F., the alloy was allowed to melt 25 min. at 730° to 680° F., and then mixed 3 min. at 680° F. The formed dross was removed at 660° F. and pressed in a hand-operated screw press, allowing the lead squeezed out to drain back into the kettle.

The second addition was made at 685° F., the alloy was allowed to melt 45 min. at 685° to 630° F., and then mixed 3 min. at 690° F. The formed dross was removed at 660° F. and pressed in a hand-operated screw press, allowing the lead squeezed out to drain back into the kettle.

After the removal of the second dross, the metal bath was allowed to cool to freezing, and the dross, crust and rim formed on cooling were removed.

TABLE 9.—*Calculation of Magnesium-bismuth Compound Ratio in Drosses Formed and Removed at* 660° *F. in Test Indicated in Table* 8

	Total Contents, Lb.		Contents of Metal Mechanically Held in Dross, Lb.		Compound Content in Dross, by Difference, Lb.	
	Bi	Mg	Bi	Mg	Bi	Mg
First dross	1.953	0.327	0.181	0.016	1.772	0.311
Second dross	2.620	0.457	0.110	0.030	2.510	0.427
					4.282	0.738

$$\text{Ratio of Bi to Mg in compound present in dross} = \frac{4.282}{0.738} = 5.80$$

$$\text{Ratio of Bi to Mg in compound } Mg_3Bi_2 = \frac{416.0}{72.96} = 5.70$$

Table 10 is a magnesium addition table for large-scale commercial operations for treatment of the higher bismuth-bearing bullions. Reduction to 0.7 per cent bismuth is contemplated, at which point final debismuthizing is completed by the combined calcium-magnesium process next to be described.

TABLE 10.—*Magnesium Required to Produce Lead Containing* 0.7 *Per Cent Bismuth*[a]

Original Bismuth Content, Per Cent	Magnesium Required, Lb. per Ton	Original Bismuth Content, Per Cent	Magnesium Required, Lb. per Ton
6.0	20.4	3.5	13.9
5.5	19.1	3.0	12.6
5.0	17.8	2.5	11.3
4.5	16.5	2.0	9.9
4.0	15.2	1.5	8.5

[a] This table is applicable only to lead containing less than 0.01 per cent combined arsenic plus antimony.

Effect of Impurities

Magnesium will remove both antimony and arsenic to a content of less than 0.01 per cent before any appreciable elimination of bismuth is obtained. Our results indicate the formation of compounds Mg_3Sb_2 and Mg_3As_2.

Zinc has no appreciable effect on magnesium.

Our experience with lead containing 0.001 per cent copper or less indicates no removal of copper by the addition of magnesium.

Silver in desilverized lead is practically unaffected.

III. DEBISMUTHIZING WITH CALCIUM AND MAGNESIUM

As previously shown, debismuthizing with magnesium alone is applicable only to high bismuth-bearing bullions, and debismuthizing with calcium alone has distinct limitations, particularly by reason of insufficient removal of bismuth. On the other hand, the use of both calcium and magnesium is the basis of our present commercial practice and effects a marked improvement over the use of calcium alone.

The bismuth content of the final lead can be reduced much lower by using both calcium and magnesium than by using either alone. As both compounds, Ca_3Bi_2 and Mg_3Bi_2, appear in the dross, apparently the presence of both reagents creates a mutually greater insolubility of both compounds. However, in very low bullions—that is, 0.05 per cent bismuth and less—the function of magnesium appears to be mainly that of decreasing the solubility of Ca_3Bi_2. This is illustrated by Table 11, which shows the effect of adding magnesium to lead containing 0.049 per cent bismuth and 0.08 per cent calcium.

When calcium is added in increasing amounts to lead containing definite amounts of magnesium and bismuth, the effect is to first debismuthize to a certain limit, depending upon the original magnesium content; thereafter, further additions of calcium result in no further removal of bismuth, but simply pass into the dross (Table 12).

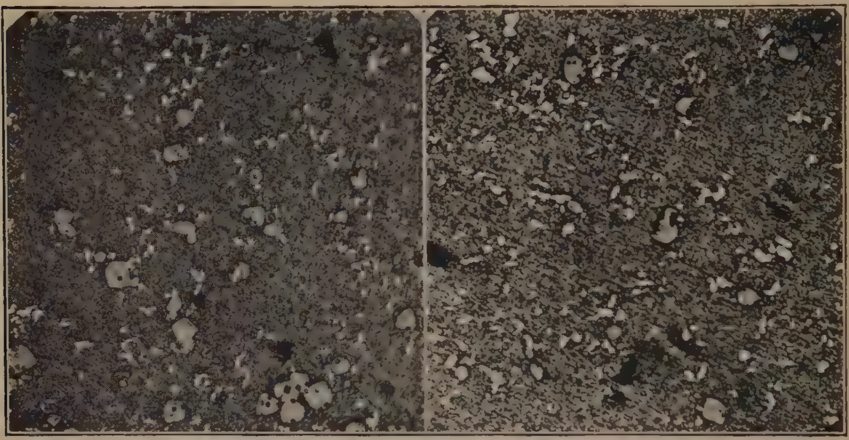


Fig. 4. Fig. 5.

Figs. 4 and 5.—Bismuth drosses. × 75.

Fig. 4. Dross from test 1, Table 14. Bi, 6.89 per cent; Ca, 1.36; Mg, 0.43.

Fig. 5. Dross from test 2, Table 14. Bi, 5.49 per cent; Ca, 0.75; Mg, 0.57.

The rather fine-grained light constituent is Mg_3Bi_2. The darker constituent tending to rhombic shape is Ca_3Bi_2. The small spots contained within these grains often are points where decomposition has set in. Fig. 4, it will be noted, contains considerably more Ca_3Bi_2 than Fig. 5. The dark spots are voids or oxide inclusions.

Compound Ca_3Bi_2.—Melting point, 1702° F. Rhombic and coarse in size. Brownish in color with slight purplish tint on standing. Moderately hard and somewhat brittle. Decomposes readily.

Compound Mg_3Bi_2.—Melting point 1319° F. Fine globular and irregular in shape. Light gray in color, tarnishing on long standing. Hard. Fairly stable.

Table 11.—*Addition of Magnesium to Lead Containing Calcium and Bismuth*[a]

Analysis Metal before Magnesium Addition, Per Cent		Magnesium Addition, Lb. per Ton	Percentage of Original Metal, by Weight, Frozen as Crust	Analysis of Metal Withdrawn from under Frozen Crust, Per Cent			Magnesium Distribution, Per Cent of Addition	
Bi	Ca			Bi	Ca	Mg	To Metal	To Crust
0.049	0.080	1.0	24.5	0.030	0.076	0.048	72.0	28.0
0.049	0.080	2.0	29.1	0.019	0.076	0.094	66.6	33.4
0.049	0.080	3.0	37.2	0.009	0.074	0.145	60.6	39.4
0.049	0.080	5.0	42.7	0.005	0.072	0.240	55.1	44.9

[a] Two hundred pounds of calcium-bearing lead was used in each test. Magnesium was introduced by placing magnesium metal turnings in a perforated basket and submerging the basket under the surface of the bath at 680° F. Upon solution of magnesium, the metal was mixed for 3 min. at 670° F. The metal was then allowed to cool to freezing. At the freezing temperature the molten metal was withdrawn from under the frozen crust through a special spout and spigot arrangement attached to the bottom of the kettle.

TABLE 12.—*Addition of Calcium to Lead Containing Magnesium and Bismuth*[a]

Analysis Metal before Calcium Addition, Per Cent		Calcium Addition, Lb. per Ton	Percentage of Original Metal, by Weight, Frozen as Crust	Analysis of Metal Withdrawn from under Frozen Crust, Per Cent			Calcium Distribution, Per Cent of Addition	
Bi	Mg			Bi	Ca	Mg	To Metal	To Crust
0.052	0.075	1.0	21.4	0.025	0.043	0.050	67.4	32.6
0.052	0.075	2.0	28.1	0.023	0.070	0.046	50.3	49.7
0.052	0.075	3.0	31.0	0.024	0.070	0.045	32.2	67.8
0.052	0.075	5.0	38.7	0.023	0.070	0.043	17.2	82.8

[a] Two hundred pounds of magnesium-bearing lead was used in each test. Calcium was introduced by placing the required quantity of calcium-lead alloy, containing 3.01 per cent calcium and 0.1 per cent bismuth, into a perforated basket and submerging the basket under the surface of the bath at 680° F. After a melting period, the metal bath was mixed for 5 min. at 680° F. The metal was then allowed to cool to freezing. At the freezing temperature the molten metal was withdrawn from under the frozen crust through a special spout and spigot arrangement attached to the bottom of the kettle.

TABLE 13.—*Joint Addition of Magnesium and Calcium to Lead Containing Bismuth*[a]

Reagent Addition, Lb. per Ton	Test 1	Test 2	Test 3
	Ca 1.5, Mg 0.5	Ca 1.0, Mg 1.0	Ca 0.5, Mg 1.5
Original bismuth content of metal, per cent	0.17	0.17	0.17
Dross, by weight, removed after reagent addition at 660° F., per cent	4.8	8.2	8.9
Calculated content of dross, per cent:			
Bismuth	1.8	1.2	1.2
Metal contents after dross removed at 650° F. per cent:			
Bismuth	0.089	0.076	0.069
Calcium and magnesium	Not determined	Not determined	Not determined
Cooling dross and rim removed on cooling to practically freezing temperature, per cent	8.9	8.2	8.2
Metal contents after cooling dross and rim removed, per cent:			
Bismuth	0.064	0.044	0.045
Calcium	0.045	0.034	0.005
Magnesium	0.019	0.036	0.053

[a] Calcium-lead alloy containing 3.01 per cent calcium and 0.10 per cent bismuth was used in above tests. Procedure followed was the same as described for tests indicated in Table 14.

Tables 13 and 14 show clearly that a ratio of calcium to magnesium of approximately one to one is the most effective proportion of these reagents to use. Calculations in Table 15 indicate that both the magnesium and calcium are effective debismuthizing reagents, forming their respective compounds with bismuth, Mg_3Bi_2 and Ca_3Bi_2.

TABLE 14.—*Joint Addition of Magnesium and Calcium to Lead Containing Bismuth*[a]

Reagent Addition, Lb. per Ton	Test 1	Test 2	Test 3	Test 4
	Ca 2.57, Mg 0.83	Ca 1.99, Mg 1.13	Ca 1.35, Mg 1.54	Ca 0.70, Mg 1.81
Weight original lead bath, lb.	193.0	198.9	200.7	199.1
Original bismuth content of metal, per cent	0.400	0.400	0.400	0.400
Dross, by weight, removed after reagent addition at 660° F., per cent	5.2	6.5	8.9	9.2
Calculated content of dross, per cent:				
Bismuth	6.89	5.49	3.96	3.55
Calcium	1.36	0.75	0.43	0.33
Magnesium	0.43	0.57	0.47	0.48
Metal contents after dross removed at 645° F., per cent:				
Bismuth	0.064	0.062	0.059	0.087
Calcium	0.058	0.052	0.031	0.005
Magnesium	0.019	0.022	0.035	0.050
Cooling dross and rim removed on cooling to practically freezing temperature, per cent	23.3	31.5	39.0	32.5
Metal contents after cooling dross and rim removed, per cent:				
Bismuth	0.053	0.050	0.042	0.085
Calcium	0.057	0.051	0.030	Tr.
Magnesium	0.016	0.019	0.031	0.046

[a] Calcium-lead alloy containing 2.23 per cent calcium and 0.37 per cent bismuth was used in these tests. The required quantities of magnesium metal and calcium-lead alloy were placed in a perforated basket and submerged under the surface of the metal bath at 680° F. Upon dissolution of the reagents, the metal in the kettle was mixed for 5 min. at 660° F. The bath was then allowed to cool to freezing and the additional formed drosses and the solidified rim on the inside circumference of the kettle were removed. The metal bath was then reheated, the kettle sides well scraped, and this dross also removed.

The photomicrographs of Figs. 4 and 5 show the presence of both compounds in the drosses removed from tests 1 and 2, Table 14.

TABLE 15.—*Calculations to Show that Bismuth Contained in Drosses Removed at* 645° *F. in Tests Indicated in Table* 14 *Is Present as Compounds* Ca_3Bi_2 *and* Mg_3Bi_2

	Test 1	Test 2	Test 3	Test 4
Total dross contents, lb.:				
Bismuth	0.689	0.709	0.717	0.650
Calcium	0.136	0.097	0.077	0.061
Magnesium	0.043	0.070	0.087	0.088
Calculated contents of metal mechanically held in the dross, lb.:				
Bismuth	0.006	0.007	0.010	0.016
Calcium	0.006	0.006	0.005	0.001
Magnesium	0.002	0.002	0.006	0.009
Compound contents of dross by difference, lb.:				
Bismuth	0.683	0.702	0.707	0.634
Calcium	0.130	0.091	0.072	0.060
Magnesium	0.041	0.068	0.081	0.079
Calculated bismuth content of dross if present as Ca_3Bi_2 based on compound calcium content as determined above	0.451	0.314	0.249	0.207
Calculated bismuth content of dross if present as Mg_3Bi_2 based on compound magnesium content as determined above	0.234	0.388	0.462	0.450
Total compound bismuth content of dross as calculated on basis of formation of compounds Ca_3Bi_2 and Mg_3Bi_2	0.685	0.702	0.711	0.657

Tables 16 and 17 show the reagent efficiencies, using a one to one ratio, and also the extent of the bismuth removal for reasonable quantities of reagent. In tests of Table 16 the final metal was withdrawn from under a heavy frozen crust. Tests of Table 17 parallel those of Table 16 except that the procedure used corresponds to the practical application for the use of both reagents in debismuthizing. Drosses in this case are removed by skimming and are less in weight, although the bismuth and calcium contents of the final metal are somewhat higher.

Table 18 shows the effect of temperature on the separation of bismuthide compounds from lead. For the grade of lead used, the maximum elimination of bismuth occurred at temperatures below 700° F.

TABLE 16.—*Joint Addition of Calcium and Magnesium to Lead Containing Bismuth*[a]

Bismuth in Original Metal, Per Cent	Reagent Addition, Lb. per Ton		Percentage of Original Metal, by Weight, Frozen as Crust	Analysis of Metal Withdrawn from under Crust, Per Cent			Calcium Distribution, Per Cent		Magnesium Distribution, Per Cent	
	Ca	Mg		Bi	Ca	Mg	To Metal	To Crust	To Metal	To Crust
0.17	1.0	1.0	28.9	0.042	0.030	0.037	43.0	57.0	53.0	47.0
0.17	2.0	2.0	32.9	0.013	0.067	0.083	47.5	42.5	58.5	41.5
0.17	3.0	3.0	39.7	0.010	0.060	0.135	26.0	74.0	59.0	41.0
0.17	5.0	5.0	47.2	0.005	0.052	0.235	12.8	87.2	57.8	42.2

[a] Two hundred pounds of lead was used in each test. Calcium-lead alloy containing 3.08 per cent calcium and 0.10 per cent bismuth was used. The reagents were introduced as described for tests indicated in Table 14. Following the introduction of the reagents the metal was allowed to cool to freezing. At the freezing temperature the molten metal was withdrawn from under the frozen crust through a special spout and spigot arrangement attached to the bottom of the kettle.

TABLE 17.—*Joint Addition of Calcium and Magnesium to Lead Containing Bismuth*[a]

Bismuth in Original Metal, Per Cent	Reagent Addition, Lb. per Ton		Percentage of Original Metal Removed as Dross and Rim on Cooling to Freezing	Analysis Final Metal, Per Cent			Calcium Distribution, Per Cent		Magnesium Distribution, Per Cent	
	Ca	Mg		Bi	Ca	Mg	To Metal	To Dross	To Metal	To Dross
0.17	1.0	1.0	17.0	0.046	0.035	0.036	59.5	40.5	61.2	38.8
0.17	2.0	2.0	17.2	0.016	0.079	0.080	68.0	32.0	69.0	31.0
0.17	3.0	3.0	20.0	0.013	0.089	0.141	50.3	49.7	80.0	20.0
0.17	5.0	5.0	22.5	0.009	0.086	0.242	29.5	70.5	83.2	16.8

[a] Two hundred pounds of lead was used in each test. Calcium-lead alloy containing 2.97 per cent calcium and 0.10 per cent bismuth was used. The reagents were introduced as described for tests indicated in Table 14. Following the introduction of the reagents the metal was allowed to cool to freezing. The drosses formed upon the addition of reagents and on cooling and also the solidified rim of metal and dross on the inside circumference of the kettle, were removed. The metal bath was then reheated, the kettle sides well scraped, and this dross also removed.

Table 19 is a reagent requirement table based on our experience for various grades of bismuth-bearing lead to produce lead of about 0.020 per cent bismuth final content.

Operating Procedure

On the basis of the results of laboratory experiments and initial large-scale tests, we have developed a standardized operating procedure for removing bismuth from lead. This procedure has been successfully

TABLE 18.—*Effect of Temperature of Bath*[a]

(Calcium and magnesium addition equivalent to 1 lb. per ton each at 800° F.)

	Percentage of Original Metal Removed as Dross	Analysis of Metal, Per Cent			Calc. Analysis of Dross Removed, Per Cent			Calcium Distribution, Per Cent		Magnesium Distribution, Per Cent	
		Bi	Ca	Mg	Bi	Ca	Mg	To Metal	To Dross	To Metal	To Dross
Original bath		0.155									
Dross skimmed at 800° F.	3.5				0.37	0.08	0.06		6.0		4.0
Bath at 800° F. after skimming dross		0.146	0.048	0.049				94.0		96.0	
Dross skimmed from 800° to 750° F.	2.1				0.21	0.10	0.05		4.0		2.0
Bath at 750° F. after skimming dross		0.143	0.047	0.049				90.0		94.0	
Dross skimmed from 750° to 700° F.	2.2				0.91	0.10	0.23		4.0		12.0
Bath at 700° F. after skimming dross		0.126	0.046	0.044				86.0		82.0	
Dross skimmed from 700° to 650° F.	2.7				2.0	0.22	0.26		12.0		12.0
Bath at 650° after skimming dross		0.070	0.040	0.038				74.0		70.0	
Cooling dross and rim removed from 650° F. to freezing	6.6								12.0		14.0
Bath after cooling dross removed		0.045	0.036	0.035				62.0		56.0	

[a] Calcium-lead alloy containing 3.01 per cent calcium and 0.10 per cent bismuth was used in the above test. The alloy and metallic magnesium turnings were submerged in a perforated basket at 800° F. Upon dissolution of the reagent, the metal bath was stirred for 3 min. at 800° F. Two hundred pounds of lead was used for this test. The operations following the introduction of reagents are indicated in the tabulation.

TABLE 19.—*Reagent Addition Table to Produce Lead of* 0.020 *Per Cent Bismuth Grade*[a]

Bismuth in Original Metal, Per Cent	Reagent Addition for Unit Ton of Lead Treated, Lb. per Ton		Bismuth in Original Metal, Per Cent	Reagent Addition for Unit Ton of Lead Treated, Lb. per Ton	
	Calcium	Magnesium		Calcium	Magnesium
0.10	1.3	1.3	0.60	2.4	2.4
0.20	1.5	1.5	0.70	2.65	2.65
0.30	1.7	1.7	0.80	2.9	2.9
0.40	1.9	1.9	0.90	3.15	3.15
0.50	2.15	2.15	1.00	3.4	3.4

[a] This table is applicable only to lead containing less than 0.01 per cent combined arsenic plus antimony.

applied to treating many thousands of tons of lead during the past year and is being used currently. Following is a short description of this method by steps:

1. Deliver softened, desilverized and dezinced lead to kettle. We normally use kettles of 225 tons capacity for this purpose. Antimony plus arsenic content of this lead should not exceed about 0.02 per cent in order to assure a satisfactory efficiency of the reagents with respect to bismuth removal.

2. The presence of any drosses of oxidizing nature is very detrimental to the efficiency of this process and they are, therefore, carefully removed by skimming when the kettle is filled with lead.

3. A small ring of frozen metal and dross formed on cooling (termed the "cooling" dross), the dross formed following the reagent addition (termed the "reagent" dross) and the "bismuth" dross, if any on hand, all from the preceding charge, are added to the molten lead in the kettle at about 790° F., following the removal of the oxide drosses.

4. The returned drosses, following a short period allowed for melting, are stirred with a lead mixer until thoroughly incorporated at about 780° F.

5. Following the mixing of the drosses, the surface of the lead bath is skimmed clean of formed dross at about 750° F. This dross is called the "bismuth" dross. If the bismuth content of this dross is about 20 per cent, as determined by the appearance of a fracture and the previous history, that is, the number of times circulated, the dross is taken out of the system and treated for the recovery of bismuth. If the bismuth content is much less than 20 per cent, this dross is returned to the following charge with the "cooling" and the "reagent" drosses as indicated in step 3 of the process. The number of times the "bismuth" dross is circulated normally depends upon the original grade of the lead debismuthized. If the lead contains about 0.5 per cent bismuth the "bismuth" dross is returned twice, and if the lead contains about 0.1 per cent bismuth, the dross is circulated three or four times. On prolonged standing, especially in contact with moist air, the compounds in the "bismuth" dross are apt to become oxidized to some degree and the circulation of this partly decomposed dross will yield no further concentration of the bismuth content in the dross. For this reason the circulation of the "bismuth" dross should also be regulated by the time elapsing between charges. When many days elapse between charges the circulation of the "bismuth" dross should be omitted and the operators must be satisfied with a lower bismuth content of the "bismuth" dross removed from the system.

6. After the "bismuth" dross is removed, the required quantity of calcium and magnesium reagents is added. The magnesium is added in the form of a cast metal, cylindrical in shape, and is incorporated by submerging in a special perforated basket and impinging a stream of lead from a pump thereon to facilitate and hasten the dissolution and reaction.

The calcium is added in the form of a calcium-lead alloy containing about 3 to 4 per cent calcium.* This alloy is added to the surface of the bath at the time the magnesium metal is submerged. The specific gravity of this alloy is less than that of lead, and for this reason it will float on the surface of the molten lead bath.

The bismuth content of the original lead treated and the desired bismuth content of the final lead must be known before the reagent addition can be accurately calculated.

Table 19 shows the calcium and magnesium requirements, expressed in pounds per ton, to produce lead of 0.020 per cent bismuth grade from lead of variable original bismuth content. From this table the calcium and magnesium reagent requirements, in pounds per ton, to produce lead of 0.020 per cent bismuth content from lead of the same bismuth grade as the lead to be treated, are easily determined. Multiplying these figures by the tonnage of new lead in the kettle, the total amount of reagents needed in pounds is computed.

7. After the magnesium is completely dissolved and the calcium-lead alloy on the surface of the lead bath somewhat softened by the influence of the heat of the metal, the charge is mixed with a lead mixer to secure contact between the various components. Normally about 30 min. of mixing at about 690° F. is sufficient. Prolonged stirring should be carefully avoided, because this results in the formation of excessive quantities of dross, thus lowering the average bismuth grade of the total dross produced. Lead containing calcium and/or magnesium drosses readily when stirred, even at low temperatures, irrespective of the bismuth content. This condition is probably caused by the incipient oxidation of the calcium and/or magnesium, the formed oxides mechanically entangling large quantities of metallic lead, thus forming a dross. This condition is further aggravated by the strong affinity of the oxygen for the alkaline-earth metals and magnesium as indicated by the heat of formation of the corresponding oxides.

8. The dross formed following the reagent addition and mixing is removed at about 690° to 670° F. This dross is termed the "reagent" dross and is returned to the following charge as indicated in step 3 of the process.

9. The lead bath after the removal of the "reagent" dross is allowed to cool to practically the freezing temperature. The kettle sides are thoroughly scraped during this cooling period. The dross formed on cooling and a small ring of dross and metal frozen on the inside circumference of the kettle are removed. This dross is termed the "cooling"

---

* Methods for manufacturing the alloy are disclosed in U. S. Letters Patent Nos. 1860524; 1941534; and 1941535, owned by the American Smelting and Refining Company.

dross and is returned to the following charge as indicated in step 3 of the process.

10. The lead bath is reheated and the kettle sides scraped again. Any dross formed is removed and returned to the following charge with the "cooling" dross.

These steps complete the debismuthizing with calcium and magnesium. At this point, if the quantity of reagents as indicated in Table 19 was used, the metal bath will contain about 0.020 per cent bismuth and normally less than 0.05 per cent of calcium and magnesium, depending upon the original grade of the lead treated.

The loss of reagents in the final lead can be controlled within certain limits, particularly by the use of minimum amounts of reagents. For this reason our practice is always to add the least possible amount of reagents necessary to obtain the desired bismuth content in the final lead.

The residual reagents, calcium and magnesium, must be removed to produce refined lead of satisfactory purity. This may be accomplished in several ways; for example, by chloridization, either with chlorine gas or suitable metal chlorides, or by oxidation, either with caustic and niter, air or steam.

Recovery of Bismuth from "Bismuth" Dross

As described in step 5 of the operating procedure, the bismuth eliminated from lead is removed in the form of a metallic dross termed the "bismuth" dross. This dross normally contains about 20 per cent bismuth, 2 to 3 per cent each of calcium and magnesium, and the balance lead. Antimony and arsenic also will concentrate in this dross if originally present in the lead debismuthized. The bulk of the lead in this dross is apparently present as metallic lead mechanically intermixed with the bismuthide compounds.

If this dross is melted with a minimum of oxidation under a cover of alkaline-earth chloride salts containing a small amount of sodium chloride, a separation is obtained, on cooling, between the metallic lead mechanically held in the dross and the calcium and magnesium bismuthide compounds.

About 75 per cent of the lead originally present in the "bismuth" dross is recovered as liquated metal containing only a small amount of bismuth. This metal is returned to the debismuthizing operations for the recovery of bismuth again in the form of a "bismuth" dross. The circulation of bismuth normally approximates 8 per cent by weight of the total bismuth contained in the "bismuth" dross liquated.

The bismuthide compounds thus greatly concentrated, and containing about 50 per cent bismuth, 5 per cent each of calcium and magnesium, and 35 per cent lead, are removed and further concentrated and refined for the ultimate recovery of refined bismuth.

IV. Debismuthizing to Very Low Limits with Antimony*

With calcium alone, the bismuth content of lead can be economically reduced on a commercial scale to 0.045 to 0.05 per cent bismuth. Using both calcium and magnesium this same limit is approximately 0.020 per cent bismuth. However, in many instances a final lead of much lower bismuth content is desired.

Comparatively recently, we discovered that two elements closely related to bismuth in the Periodic System—arsenic and antimony—exert certain extremely beneficial effects when added to lead under proper conditions. For instance, when a suitable quantity of antimony is added to lead containing small amounts of bismuth, and also calcium and magnesium, within an appropriate temperature range, a dross is obtained in which the bismuth, antimony, calcium and magnesium are concentrated, thus making possible the production of a final lead of very low bismuth content. The antimony addition is governed by the bismuth content of the bath, and for definite temperatures drosses are obtained with fixed ratios of their constituent metals; namely, bismuth, calcium, magnesium and antimony. It will thus be apparent that antimony acts chemically in the further removal of bismuth to very low limits.

This process is now commercial for the production of final lead containing 0.005 per cent and less of bismuth, and experimentally we have produced lead containing as low as 0.0005 per cent bismuth. It can be applied either to new bullion or to lead previously debismuthized with alkaline earth metals including magnesium and after no further debismuthizing can be effected with these reagents.

---

* See U. S. Letters Patent No. 2056164.

Continuous Lead Refining at Port Pirie, South Australia

By G. K. Williams*

The continuous process of lead refining as at present operated at the Port Pirie plant of The Broken Hill Associated Smelters Proprietary Ltd. was a development from investigations conducted in connection with the ordinary Parkes desilverizing process.

It is not proposed here to discuss the theoretical considerations involved in continuous desilverizing because this aspect has already been dealt with in previous publications.[1]

CONTINUOUS SOFTENING PROCESS

For economical desilverization of lead bullion, the bullion must first be subjected to refining processes for the removal of such impurities as copper, sulphur, arsenic, antimony and tin. This refining is effected by first drossing to remove copper and sulphur and then preferentially oxidizing the arsenic, antimony and tin from the bullion in the softening process.

The theoretical basis of the continuous softening process is illustrated by the portion of the Pb-Sb-O ternary equilibrium diagram shown in Fig. 1. Under conditions of complete liquefaction, metal of the composition of softened bullion is in equilibrium with an oxide slag containing about 9 per cent antimony. In practice, of course, arsenic also is always present, and while the Pb-Sb-As-O quaternary system has not been worked out in detail, it has been found that in softening drossed smelter bullion of the composition produced at Port Pirie, arsenic is always reduced to 0.001 per cent or less when the antimony in the bullion is reduced to a satisfactory figure.

In the operation of the continuous softening process, a two-phase system of a bullion low in arsenic and antimony and an oxide slag relatively high in those components exists in equilibrium. To this system is added continuously a bullion containing 0.2 per cent As and 0.8 per

---

Manuscript received at the office of the Institute Aug. 17, 1936.

* Broken Hill Associated Smelters Proprietary Limited, Smelting Works, Port Pirie, South Australia.

[1] G. K. Williams: Description of Continuous Lead Refinery at the Works of The Broken Hill Associated Smelters Proprietary Limited, Port Pirie, South Australia. *Proc.* Aust. Inst. Min. & Met. (1932) [N.S.] No. 87.

G. K. Williams: Thesis on The Development and Application of the Continuous Lead Refining Process.

cent Sb and a gas (air) containing oxygen, this addition of oxygen being controlled at such a rate that the arsenic and antimony in incoming bullion are oxidized with some lead in such proportions that more slag of the composition already existing in equilibrium with the bullion bath is formed. Slag and softened bullion are withdrawn from the system continuously and a state of dynamic equilibrium is maintained.

Thus continuous softening does not differ from batch softening in the respect that it depends on the preferential oxidation of arsenic and antimony and the formation in this way of an oxide slag relatively rich in these two impurities, but it has the obvious advantage over the batch process that the following typical delays are eliminated from the furnace-operating schedule: (1) time lost in filling furnace; (2) time lost in attaining optimum temperature for the operation; (3) time lost in cooling back prior to skimming; (4) time lost in skimming; (5) time lost in emptying the furnace.

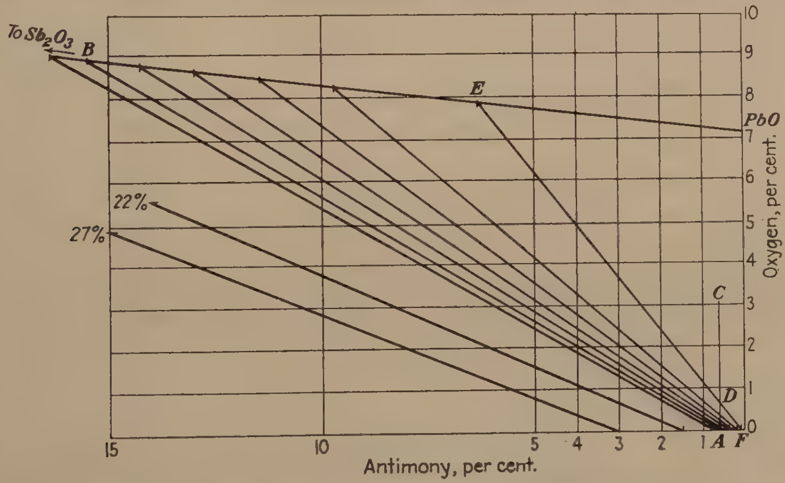


FIG. 1.—PORTION OF LEAD-ANTIMONY-OXYGEN TERNARY EQUILIBRIUM DIAGRAM.

In the continuous process the furnace is charging and discharging while the process proceeds and liquid dross is removed continuously, the furnace temperature being maintained at the most efficient figure for the conduct of the process.

However, besides these obvious advantages, there is one less obvious, which, insofar as increasing the capacity of a furnace of any particular size is concerned, probably outweighs all others. This depends on the fact that while in the batch process the bath of metal changes in composition during the treatment of any particular batch, with the Port Pirie bullion from 0.8 per cent Sb 0.2 per cent As at the beginning of the operation to 0.02 per cent Sb and less than 0.001 per cent As at the end, in the continuous process the bath is maintained at all times at the latter figure.

Now, investigation of the rate of oxidation of a bullion bath has indicated that the rate is greatly affected by its arsenic and antimony contents in the manner shown in Fig. 2, which represents the results of a series of experiments covering the whole batch cycle. The oxidation rate of the bullion corresponding to the bath in the continuous softener is 32 times as great as that of the bullion in the bath at the commencement of a batch cycle. Also, by far the greater time during the batch process is spent with the bath composition corresponding to the low oxidation rate, since once it reaches the region of high oxidation rate it is softened and ready for withdrawal from the furnace. With the continuous process, the bath is always at a composition corresponding with very high oxidation rate, so that the oxidation of the bath, which corresponds with the softening of the bullion, proceeds at a rate many times greater than is possible in batch softening.

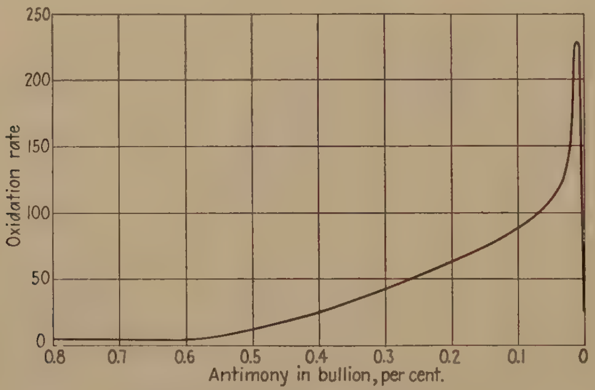


Fig. 2.—Oxidation rate versus antimony content.

Continuous Enrichment of Antimony Dross

In the continuous antimony-dross furnace, as in the softener furnace, there is present a bath of lead containing some arsenic and antimony, upon which is superimposed a layer of oxide slag in equilibrium with the metal bath. The arsenic and antimony contents of both metal and slag are considerably higher than in the softener, but the equilibrium relations indicated in Fig. 1 still hold, although here again these equilibrium relationships are affected by the presence of arsenic in the system.

Whereas the process in the softener furnace was one of oxidation, that in the antimony-dross furnace is one of reduction, antimony dross from the softener furnace and small coal being added simultaneously to the furnace, which contains the two-phase system described above.

As a result of the reactions between the reducing agents in the coal added and the lead, arsenic and antimony in the softener slag, reduction of these these metals from their oxides proceeds, and the proportions of the metals reduced are such that more slag and more metal, of the compositions of those already in the furnace, are produced. Thus, as in the softener furnace, a state of dynamic equilibrium obtains.

Metal, relatively low in arsenic and antimony, and slag relatively high in these components are withdrawn continuously from the furnace.

CONTINUOUS REFINING FOR ZINC

Like the continuous softening process, the continuous zinc-refining process takes advantage of the exceptionally high oxidation rate of nearly pure lead and embodies a molten lead bath covered by a layer of molten oxide slag. Desilverized lead is added to the furnace continuously and refined lead and liquid oxide slag are continuously withdrawn. The refiner slag contains arsenic and antimony in much the same proportions as the softener slag, but it also contains about 8 to 10 per cent zinc. A slag of this composition is in equilibrium with a bullion sufficiently low in arsenic, antimony and zinc to fulfill the specifications for refined lead.

The presence of zinc in the slag raises its melting point, so that a somewhat higher temperature is required in the refiner than in the softener furnace.

The presence of arsenic and antimony in the slag is required in order to so lower the melting point that a liquid slag can be run off freely and continuously from the furnace. Enriched antimonial slag from the continuous antimony-dross furnace is added to the refiner in granulated form in sufficient quantity to raise the arsenic and antimony content of the refiner slag to the required figure.

Despite the large proportion of antimony in the refiner slag, the refined lead produced has an antimony content slightly lower than that produced by the old batch process.

CONTINUOUS REFINING AT PORT PIRIE

At Port Pirie it has always been contended that the economic practice of removing gold and silver from a softened bullion by the Parkes process depends on the quantity of copper present in the softened bullion.

If the bullion to be desilverized contains a relatively large quantity of copper, such as 0.06 per cent, the value present in the softened bullion at Port Pirie before improvements were made to drossing practice, the contaminations of copper in the alloy produced in desilverizing seriously increases the quantity of zinc used and the cost of retorting and cupellation.

With the continuous conjugate solution process, the presence of 0.06 per cent copper in the bullion to be desilverized would, in addition, adversely affect the desilverizing operations, especially as regards the liquidity of the alloy, and would also increase the costs of fuel and kettle maintenance.

Thus when the softened bullion contained 0.06 per cent copper, before improvements were effected in drossing methods, the economic practice was to first degold the bullion before desilverizing. During the degolding process copper as well as gold was removed from the bullion, the typical copper content of degolded bullion being 0.01 per cent.

With a copper content of 0.004 per cent assured for the softened bullion, degolding and desilverizing in one operation became the more economic practice.

Operating Units at Port Pirie

The layout of the continuous refinery is given in Fig. 3. The refinery is considered in six sections, the operating units of which are as follows:

Bullion-storage Section

The bullion-storage section comprises two 90-ton storage kettles.

Softening Section

1. Two softening furnaces of the water-jacketed reverberatory type (Fig. 5) 15 ft. long by 5 ft. wide, inside dimensions, with provision for operating four air agitators in each furnace.
2. Two antimony-dross furnaces, which are wide, water-jacketed reverberatory furnaces, 17 ft. long by 11 ft. wide inside dimensions, each heated by an oil burner situated in the side of the furnace near the charging end. The antimony dross is charged through a hole in the crown of the furnace near the end distant from the flue and the antimony slag and hard lead are discharged from the furnace at the opposite end.
3. One 5-ton oil-fired hard-lead kettle, arranged in a brickwork setting.

Desilverizing Section

1. Two temperature-control furnaces, which are reverberatory furnaces oil-fired by means of a burner at the discharge end.
2. Three desilverizing kettles (Fig. 7). Each kettle holds 380 tons and is made up of four independent castings; namely: (*a*) top, (*b*) conical, (*c*) cylindrical, (*d*) bottom.

The brickwork setting around the kettle is divided into nine superimposed chambers by means of brickwork arches; each of six of the chambers has two oil burners and these chambers are situated as follows: No. 1 chamber, around top casting; No. 2 chamber, around conical casting; No. 3 chamber, around cylindrical casting; Nos. 4, 5 and 6 chambers, around bottom casting. The remaining three chambers surround the three joints and are not equipped with oil burners. (Fig. 8.)

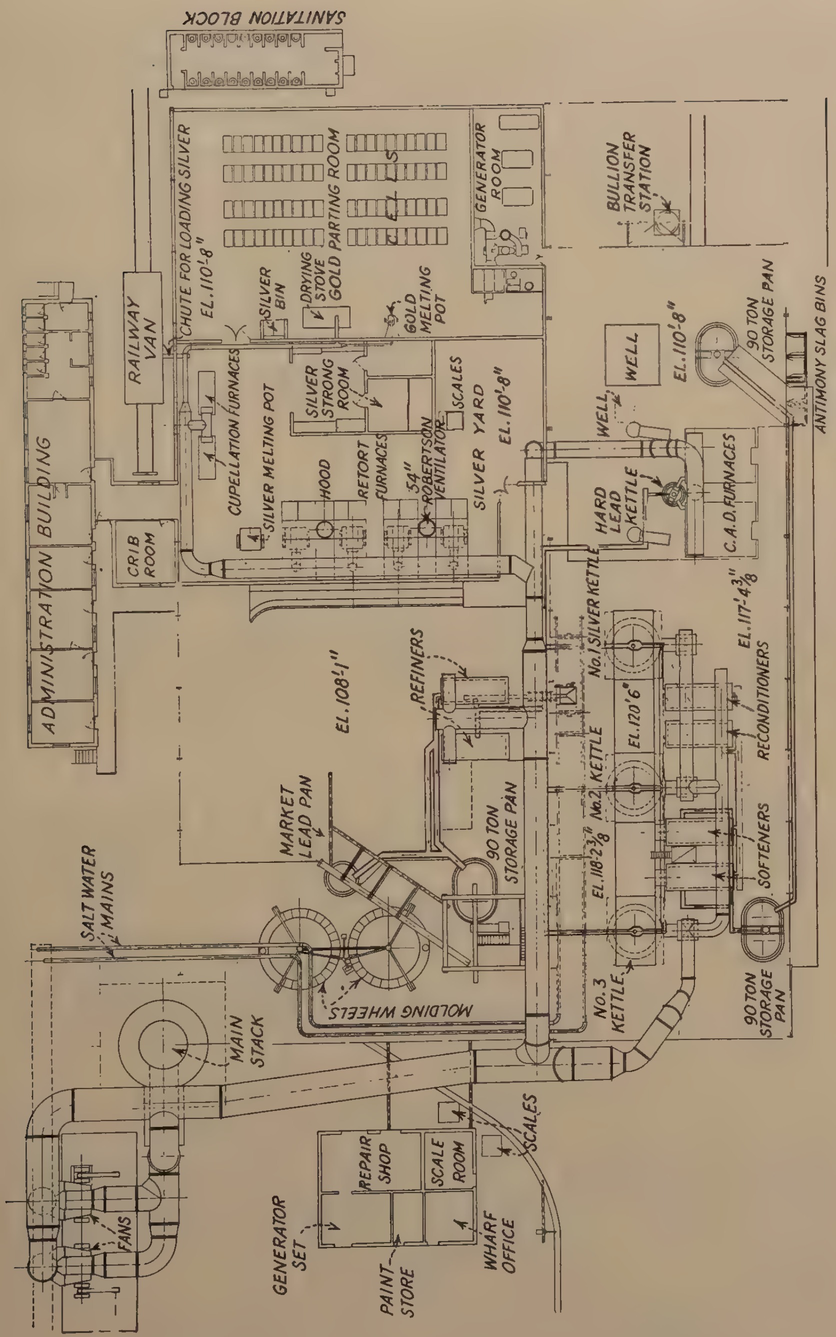


Fig. 3.—General Arrangement of Continuous Refinery.

In chambers 1 to 6 checker walls are built on each side of the kettle, parallel with the line of projection of the oil burners, and the combustion of the oil takes place on the further side of these checker walls, away from the kettle. The products of combustion pass through the openings in the checker walls around the kettle and thence to the flue.

The top casting has two projections, into one of which is welded a cast-iron box that is connected with the launder delivering bullion to the kettle, and provides, by means of an underflow lip, a submerged inflow of bullion into the kettle. By this means bullion free from dross is delivered to the kettle. The other projection is a launder for receiving the siphon pipe, which is held in position by plates welded to the top casting. This launder is well packed with chamotte around the siphon pipe, to prevent any leakage of alloy or lead from the kettle.

Zinc-refining Section

The zinc-refining section consists of two zinc-refining furnaces of the reverberatory type, water-jacketed, 15 ft. long by 5 ft. wide inside dimensions, each heated by an oil burner situated at one end of the furnace. The lead and dross are discharged from the furnace at the flue end. Each furnace is equipped with cooling water and air supply for four compressed-air agitators, which can be lowered into the furnace through holes in the crown.

Molding Section

The layout of the molding section is shown in Fig. 3. The two molding wheels are mechanically driven and are of the standard Newnam type.

Silver Yard Section

The units in the silver yard section can be grouped as follows:

1. Four retorting furnaces. These are oil-fired, of the tilting type. The bottle contained in each furnace has a holding capacity of 36 cwt. of silver-gold alloy.
2. Two cupellation furnaces. These are small reverberatory furnaces of very shallow type, oil-fired. The furnaces are water-jacketed and have litharge-overflow jackets.
3. Doré parting plant. The layout of this plant is shown in Fig. 3. The plant consists of 80 cells of the Balbach type, provided with the standard equipment for the efficient production of market gold and market silver.

METALLURGICAL OPERATIONS AT PORT PIRIE

Fig. 4 gives the diagrammatic flowsheet of the modified new refinery. The continuous flow of bullion is commenced from the higher-level storage kettle and passes in sequence through the softening furnace, the silver kettle and the zinc-refining furnace to the small storage kettle feeding the molding wheels.

The drossed smelter bullion flows continuously into the softening furnace, and the flow of metal through each of the separate units of the refinery is likewise continuous until the Newnam kettle is reached. The levels of the various units are so adjusted that the lead gravitates through each; the flow of bullion into the softener thus controls the flow throughout the refinery, and no separate adjustment is required for the individual units.

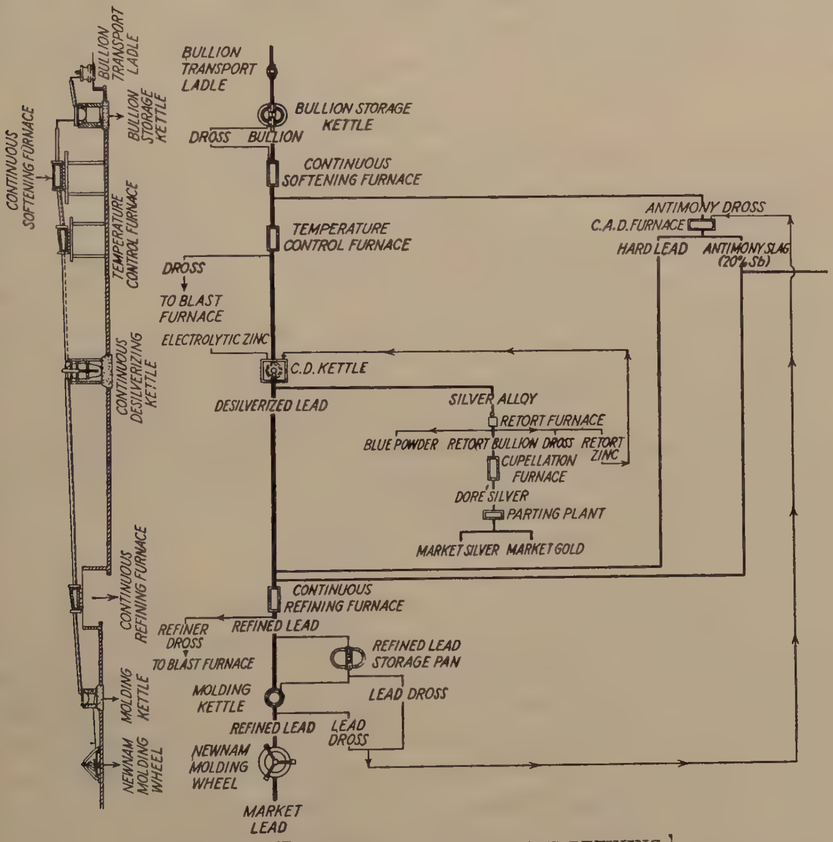


FIG. 4.—FLOWSHEET OF CONTINUOUS REFINING.

Bullion-storage Section

The drossed smelter bullion is conveyed in 15-ton ladles from the copper-drossing plant to the refinery, where it is pumped into the lower-level storage kettle of 90 tons capacity. When the pump that transfers the bullion from the 15-ton ladle to the storage kettle is not in use, it is immersed in a lead bath, which is maintained at 400° C. in a small 5-ton kettle to prevent cooling.

The bullion is transferred periodically, as required, through a launder from the lower-level storage kettle to the higher-level storage kettle of 90 tons capacity. The bullion is pumped continuously at the required rate from the higher-level storage kettle into a launder, which discharges the bullion into either of the two softening furnaces.

The typical analysis of the drossed smelter bullion delivered to the softening furnace is: Cu, 0.004 per cent; As, 0.29; Sb, 0.78; Ag, 53.1 oz. per ton; Au, 0.039 oz. per ton; S, 0.0011 per cent.

Softening Section

Some details of the continuous softening furnace are shown in Fig. 5. The drossed smelter bullion from the supply pump flows down a refractory launder (encased in steel plate) and enters the softening furnace by means of the bullion-inlet box attached to its side. As the communication between this box and the main furnaces is large (4 in. square), the lead in the box is always hot and no trouble is encountered through its freezing. Again, as the connection is situated near the bottom of the furnace, the slag cannot pass out into the bullion-inlet box.

The softened bullion flows from the furnace beneath a D-shaped jacket, which forms a siphon preventing the slag from flowing from the furnace with the bullion. The slag flows from the furnace over a notch in the water jacket, thence through a small water-jacketed launder into slag pots. Bullion and slag outlets are side by side at the end of the furnace.

The 2½-in. difference in slag and bullion overflow levels results in a layer of nearly 4 in. of slag being carried over the surface of the lead when both slag and bullion overflows are open. This ensures that, despite the agitation, no bullion escapes with the slag, and consequently the silver content of the slag is very low.

Care is taken to ensure a reasonably even flow of bullion through the furnace. The pump delivering the unsoftened bullion from the storage pan is equipped with a valve and controlling mechanism. The valve is situated close to the pump itself, and is thus always immersed in the bullion. In controlling the flow, two methods are practiced: (1) A ladle is placed under the pump overflow pipe, and the time to fill the ladle measured by means of a stop watch; (2) the storage pan is equipped with a float and gauge marked off in tons, and consequently by reading this gauge periodically and noting the time, the average flow can be deduced. In normal practice the pump works very evenly, and the second method is used except for periods in which the flow has been purposely altered for short periods, when the first method is employed.

During softening, the bullion and dross in the furnace are subjected to intense agitation by means of water-jacketed air agitators, which are introduced through holes in the crown and so submerged that the air is discharged approximately 4 in. from the bottom of the bullion bath.

The number of agitators required varies with operating conditions, such as the flow of bullion through the furnace, the state of repair of the furnace and the temperature of the bullion.

The temperature of the softened bullion as it discharges from the furnace is maintained at 760° C; the factors influencing the temperature are:

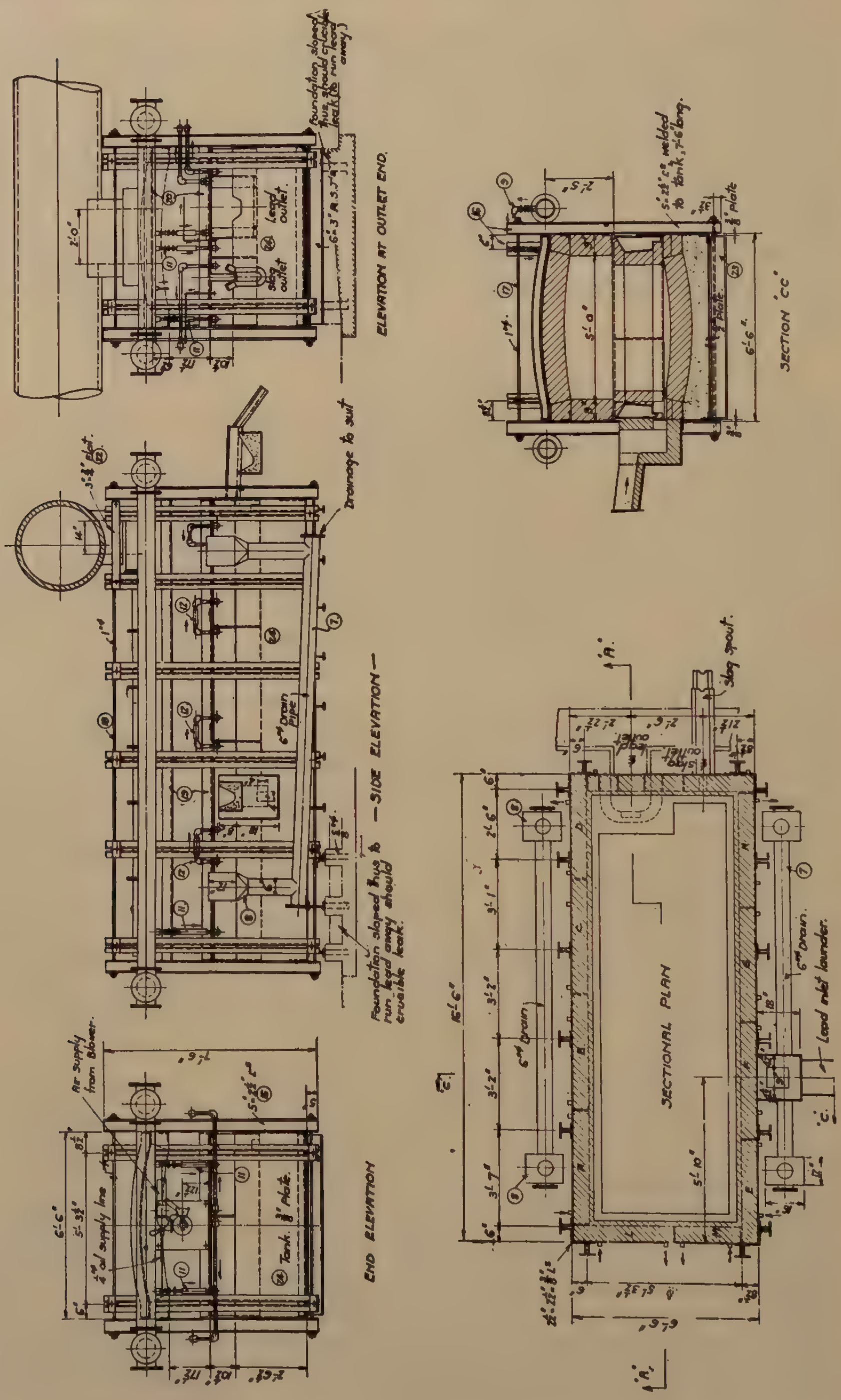
1. Rate of bullion flow.
2. Gallons of oil burned per hour.
3. Degree of agitation. The necessary heat for the operation of the softener furnace is supplied largely by the heat evolved by the exothermic reactions involved in the oxidation of lead, antimony and arsenic in the bullion. By controlling the agitation, the furnace will run for long periods without the use of any external heating.
4. Composition of the slag. The composition of the slag determines the extent to which a solid coating exists over the bare water jackets, and this has a direct bearing on the heat lost from the furnace in circulating water.

In operating the furnace, the direct controls are the rate of burning oil, the degree of agitation, and the rate of treatment, and these are manipulated both to obtain the desired temperature of 760° C. in the softened bullion as it leaves the furnace and to ensure the correct composition of the slag so that it forms a solid coating on the jacket.

In practice it has been demonstrated that the composition of the slag can vary between wide limits and yet maintain a small loss of heat in the jacket water; the limits appear to be approximately 6 and 10 per cent of antimony in the slag. The correct grade of slag can readily be determined optically by observing its tendency to solidify in contact with the water jacket, and the physical character of samples of solidified slag.

With the normal flow of 26 tons per hour and the furnaces in good repair, two agitators are required to ensure that the arsenic and antimony are oxidized at the same rate that they are introduced into the furnace in the unsoftened bullion.

If the rate of oxidation is too low as determined by either the appearance of the dross or the quantity of dross discharging from the furnace, the adjustment is either to increase the agitation or the quantity of oil being burned. If the temperature in the furnace is low with a normal quantity of oil being burned, either the agitation has been insufficient or else the grade of the dross has changed so that it is too high in antimony and, consequently, of too low a melting point, with the result that the


ELEVATION AT OUTLET END.
Foundation sloped thus, should crucible leak, to run lead away.
Lead outlet.
Slag outlet.
2'-0"
6'-3" R.S.J.
SIDE ELEVATION
Drainage to suit
6" drain pipe
Foundation sloped thus to run lead away should crucible leak.
14"
END ELEVATION
Air supply from Blower.
1/4" oil supply line
Tank. 3/8" plate.
6'-6"
7'-6"
SECTION 'CC'
5'-0"
6'-6"
2'-5"
3/8" plate
SECTIONAL PLAN
Slag spout.
Lead outlet
Slag outlet
6" drain
6" drain.
Lead inlet launder.
15'-6"
2'-6"
3'-1"
3'-2"
3'-2"
3'-7"
5'-10"
6'-6"
'A'
'C'

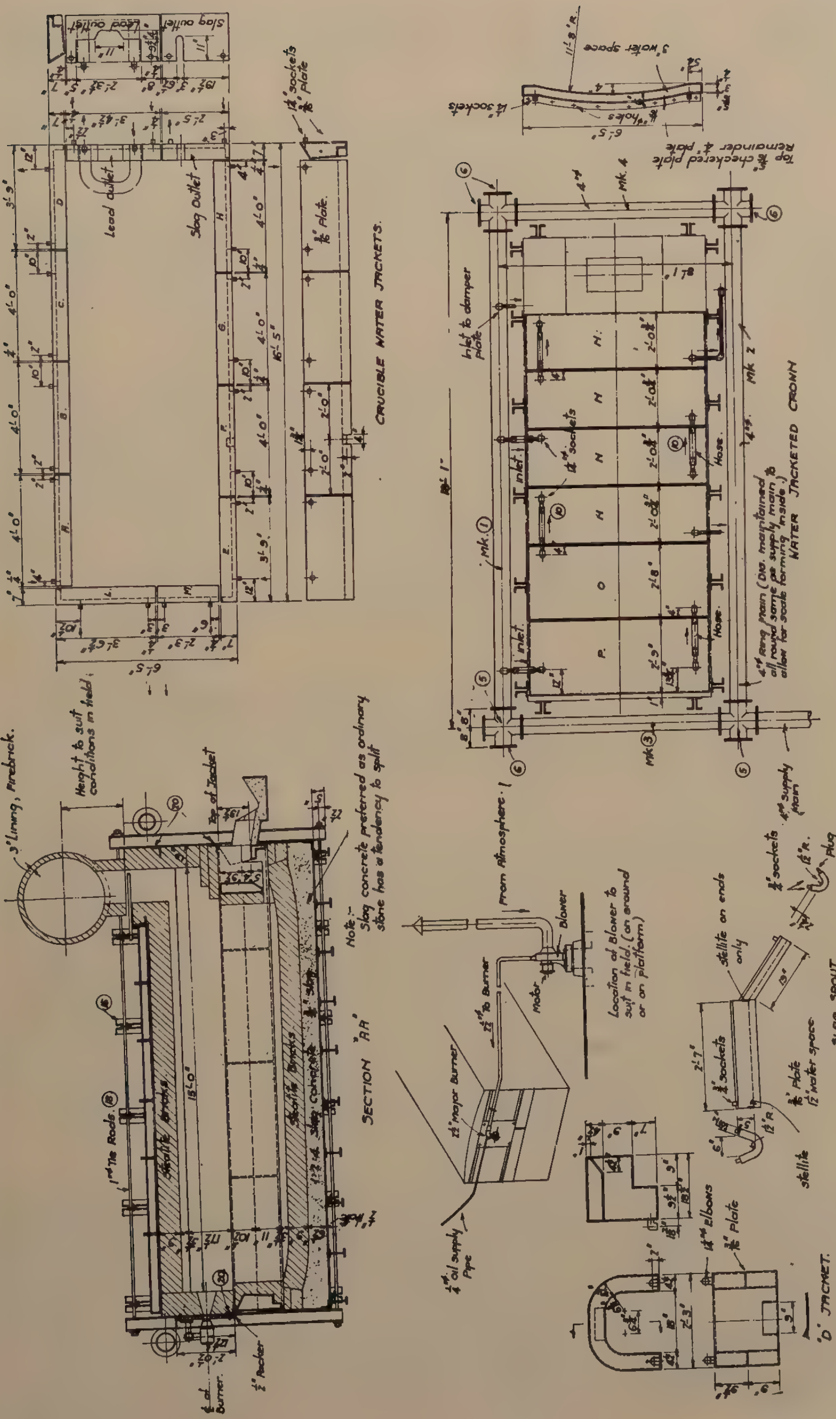


FIG. 5.—DETAILS OF SOFTENER.

water jackets have become bare. The adjustment for this is to increase the agitation or the oil usings or to decrease the flow of bullion through the furnace.

The particular adjustment chosen is dependent on the operating conditions existing and the particular requirements to be satisfied at the time.

The typical analyses for the products of this furnace are:

	Softened Bullion	Antimony Dross
Copper, per cent	0.0043	0.0052
Arsenic, per cent	0.00043	2.7
Antimony, per cent	0.03	8.1
Silver, oz. per ton	58.3	
Gold, oz. per ton	0.041	

Antimony dross flows continuously from the softener furnace down a water-cooled launder to slag pots of ½-ton capacity. These pots are wheeled to the antimony-dross furnace, which is situated at a lower level than the softener, and their contents are discharged through a hole in the top arch. The slag in the pots is usually still molten when tipped, although there is a thin, frozen shell.

Small coal is charged continuously into the furnace by means of a conveyor belt running beneath a small bin. The speed of the belt can be accurately controlled.

The reaction of the coke on the dross results in lead being preferentially reduced so that two products are formed: "Antimony slag" of relatively high antimony content, 20 to 25 per cent Sb, and "hard lead," containing about 1 per cent Sb.

One agitator only is used to give a good mixing of slag and reducing agent. The relatively high antimony content of the metal bath serves to prevent oxidation, moreover the agitator is not operated at sufficient air pressure to cause much splashing of metal. The hard lead, which flows continuously from the furnace, is stored temporarily in an oil-fired 5-ton kettle, from which it is pumped periodically to the refiner furnace.

Since the make of enriched slag is not large, it is usually allowed to build up in the furnace for some time and tapped periodically. The portion of the slag that is required for addition to the refiner is granulated by running into a water tank; the remainder is run into pots from which it is tipped into a small bin for shipment.

The main factors influencing the operation of the furnace are: (1) quantity of oil burned, (2) quantity of small coal added, (3) rate of slag addition. In practice, the oil burned is adjusted to give a temperature of 650° C. in the hard lead issuing from the furnace, the softener slag is fed in at a constant rate, and the rate of feeding the reducing agent is adjusted to give a reasonable concentration of coal over the slag furnace.

The following are typical analyses of hard lead and antimony slag:

	HARD LEAD	ANTIMONY SLAG
Arsenic, per cent	0.01	3.8
Antimony, per cent	0.64	21.9
Silver, oz. per ton	0.32	0.14
Copper, per cent	0.005	0.004

Desilverizing Section

The softened bullion flows down a refractory-lined launder to the temperature-control furnace, which serves to ensure a temperature of 650° C. in the softened bullion as it enters the desilverizing kettle (Figs. 7 and 8).

The main factors influencing the operation are: (1) temperature of softened bullion as it leaves the furnace, (2) length of launder connecting the softener and temperature-control furnace, (3) rate of bullion flow. In actual practice, the correct quantity of oil per hour is readily determined, and the quantity is maintained more or less continuously.

The bullion to be desilverized is delivered down a refractory launder at a constant rate of flow, and enters the kettle via the inlet box, which forms a partition wall across the inlet launder of the casting, followed by an underflow lip giving a submerged flow of the bullion into the kettle, so that any surface dross carried by the bullion is trapped and periodically removed.

Under operating conditions the top casting of the kettle is nearly completely filled with zinc-silver-lead alloy, which, on account of its low specific gravity, floats on the bullion that fills the other three sections of the kettle. The bullion enters the kettle proper in a wide shallow stream falling through the layer of alloy. The contact between the stream of bullion and the layer of alloy and at the surface of separation of the layers of lead and alloy results in: (1) enrichment of the alloy in silver, (2) solution of zinc in the lead.

As the enrichment of the alloy in silver proceeds, the silver content of the layer of lead immediately in contact with the alloy also increases, and ultimately, when the zinc-silver-lead alloy reaches the composition at which it is dipped out for retorting, the silver content of the bullion in contact with the alloy layer is considerably greater than that of the inflowing bullion. However, the incoming bullion absorbs sufficient zinc to ensure that in cooling to its freezing point crusts separate out, leaving a final bullion very low in silver.

As the bullion is displaced down the kettle, its temperature gradually falls until it reaches its freezing point at the entrance to the siphon pipe, where liquid and solid metal exist in equilibrium; the crusts that separate during the cooling rise to the top casting where a portion is dissolved in the incoming bullion and a portion in the zinc-silver-lead alloy layer.

After reaching the bottom of the kettle, the lead rises up the vertical siphon pipe, and flows out the horizontal branch. Since the upper part of the siphon pipe is situated in the hottest part of the kettle, the bullion becomes reheated to about 370° C. before leaving the kettle, and its disposal by means of a launder is thus facilitated.

The richness in silver of the alloy layer gradually increases from the time when the layer has been first made up until a practical limit of about 6000 oz. per ton is reached, when it is removed.

When the alloy first shows signs of solidifying on the siphon pipe, its removal is indicated. The freezing point of the alloy increases with increasing concentration of silver, thus the freezing of the alloy on the siphon pipe at a particular temperature indicates its grade. The alloy layer, which had an original depth of 3 ft., is ladled out by hand until the underlying lead is reached. The time required for the alloy to enrich to the grade of 6000 oz. per ton depends on: (1) the rate of flow of bullion through the kettle, (2) the concentration of silver in the bullion, (3) the depth of zinc alloy maintained in the kettle. Under Port Pirie conditions, the zinc alloy is dipped about once every 12 hours.

When the enriched alloy has been removed, the layer of zinc is built up again to a depth of 3 ft. The zinc is added in solid form, and the rate of addition is adjusted so as to maintain a temperature of 530° C. in the alloy layer.

Although every section of the kettle can be heated, if necessary, under normal conditions only the burners heating the top casting are continuously in operation. The temperature inside the top casting is held at 580° to 600° C., but the process involves a steady cooling throughout the remainder of the kettle to about 330° C. at the lowest point in the bottom casting.

Under correct running conditions, the bottom of the kettle is at such a temperature that a layer of solid eutectic practically free from silver gradually builds up beneath the siphon pipe, the amount of this eutectic being gauged by the vertical movement of the iron rod placed in the siphon pipe. When this movement decreases to about 3 to 4 in., the burners in No. 6 hearth are lighted and heat is applied until the movement of the measuring rod increases to about 8 to 10 in., when the No. 6 burners are shut off and eutectic begins again slowly to build up. Under Port Pirie conditions about an hour's firing is required for this purpose every 12 hours.

It is found that the crusts liberated from the cooling lead in the lower sections do not rise completely up the kettle. There is a tendency for accumulation of crusts to form on the casting at certain portions. These gradually build up, and if allowed to grow unimpeded ultimately bridge over from the kettle walls to the siphon pipe, impeding the flow of bullion through the kettle. These accretions form usually at the level of hearths Nos. 3 and 4, and by lighting the burners in those hearths periodically the crusts are freed and rise into the upper layer, where they melt, giving a liquid alloy of moderate silver content usually 2000 to 3000 oz. per ton. Because of the comparatively large quantity of low-grade alloy which thus accumulates in the top of the kettle, it is necessary to remove a certain amount by dipping to prevent the kettle from overflowing. The alloy removed, being relatively low in silver, is subsequently returned to the kettle in building up the zinc layer after dipping of high-silver alloy. During the heating of the casting for this cleaning-up process, the lead becomes heated above its normal working temperature, and it is necessary to stop the kettle for about 8 hr. afterwards to allow correct temperature conditions to be regained. This stoppage occurs once each week, and during it necessary plant repairs are made.

The cooling of the bullion in the lower section of the kettle is controlled by regulation of the cooling air drawn through chambers 2, 3, 4 and 5. Normally the dampers in the various sections are arranged as follows: Section 2, damper out and brickwork opened up; Section 3, damper closed; Section 4, damper closed and luted with clay; Section 5, damper closed and luted with clay; Section 6, damper closed except when firing to reduce accumulation of lead-zinc eutectic. This simple arrangement of drafting gives the correct temperature gradient down the kettle for normal working.

Under normal running conditions frequent assaying of the desilverized lead for silver is unnecessary, and the confidence placed in the process can be gauged by the fact that only one assay for silver is made for each 8-hr. shift, the sample being made up from eight hourly samples.

Typical analyses of the products of this section are:

	DESILVERIZED LEAD	SILVER ALLOY
Copper, per cent	0.0005	
Antimony, per cent	0.038	
Zinc, per cent	0.54	64.0
Silver, oz. per ton	0.03	6000
Lead, per cent		15.0
Gold, oz. per ton		4.2

Zinc-refining Section

The desilverized lead gravitates from the kettle along a refractory-lined launder and is delivered through a hole in the roof of the zinc-refining furnace near its center.

The market lead flows from the furnace over a notch in the water jacket, which has a D-shaped water jacket attached to its inner side. The lead flows under the D-jacket and over the notch, whereas the slag in the furnace is prevented by the D-jacket from overflowing with the lead.

The slag runs from the furnace over a special notch in the water jacket, and is discharged into an endless chain of molds. It is cooled by water sprays and tipped into skips, in which it is transported to the blast furnaces for resmelting.

In refining for zinc the fact that zinc oxidizes preferentially to lead is employed. Thus the principles involved in the purification of the desilverized lead for zinc are similar to those employed in the purification of bullion for arsenic and antimony in the softener furnace, with two important exceptions, which modify the practice.

Firstly, the zinc oxide in the slag, unlike the oxides of arsenic and antimony, does not lower the melting point, so that the slag formed by the oxidation of desilverized lead is a mixture of lead and zinc oxides, which has a high melting point and would not be liquid at temperatures at which it is convenient to operate the zinc-refining furnace. In order to obtain a liquid slag, arsenic and antimony are fed to the furnace as "antimonial slag" and "hard lead." The presence of sufficient arsenic and antimony ensures the liquidity of the slag.

Secondly, in the softener furnace the greater the make of slag the larger the amount of lead that escapes desilverizing and passes directly to the zinc-refining furnace in the form of "hard lead," and hence the less zinc consumed in desilverizing, but in the zinc-refining furnace all slag produced is returned to the blast furnaces and must be subjected to costly re-treatment; moreover, the cost of the softening and desilverizing treatment to which the lead in this slag had been subjected is lost. Hence, whereas in softening the object of the operator is to produce as much slag as possible, in refining the object is to limit the production of slag to the smallest possible tonnage. This end is achieved by limiting the agitation to give just sufficient oxidation to produce the grade of market lead required; the extra heat required is obtained by burning the necessary quantity of oil. The desired fluidity of the slag is obtained by controlling the addition of antimony slag so that the necessary antimony, over and above that introduced in the hard lead, is thus added.

From actual experience it has been determined that the quantities of antimony slag and hard lead should be such that the total antimony contained in them is equivalent to 0.4 per cent of the weight of desilverized lead treated.

In practice, no difficulty is experienced in maintaining an excellent grade of market lead and fluid slags, the accepted method being to operate with constant oil and periodically to adjust the quantity of antimony slag and degree of agitation to suit the existing conditions.

The factors influencing the operation of the furnace are: (1) quantity of oil burned per hour, (2) degree of agitation, (3) quantity of antimony slag added per hour, (4) composition of the antimony slag, (5) quantity of hard lead added per hour, (6) composition of the hard lead.

For satisfactory operation, it is desirable that the temperature maintained in the furnace shall be such that the temperature of the market lead as it leaves the furnace is approximately 780° C.

The following are average figures for refined lead and for refining-furnace slag:

Refined Lead	Per Cent
Antimony	0.0038
Bismuth	0.0007
Copper	0.0005
Iron	0.00035
Silver	0.0003[a]
Zinc	0.0002
Sulphur	0.0002
Cadmium	0.00015
Arsenic	0.000015
Tin	Nil

Refining-furnace Slag	Per Cent
Zinc	9.2
Antimony	6.9
Arsenic	1.3
Copper	0.002

[a] Equals 2 dwt. per ton.

Molding Section

The refined lead gravitates from the zinc-refining furnace down a refractory launder to a 27-ton pan, which provides storage for the operation of the two Newnam molding wheels on which the lead is molded into 90-lb. bars, the bars being picked out from the molds by hand. Special precautions, which include the heating of the upper surfaces of the bars in an oil-fired oven and the cooling of the bottom surfaces of the molds by water sprays, ensure the soundness of the bars. Tests show the bars to be free from blowholes or other cavities.

Silver Yard Section

Retorting Section.—The practice of retorting is similar to that in use in other lead refineries except that the size of the bottle has been developed from the standard size (12 cwt. holding capacity) to a much larger size (36 cwt. holding capacity). This development has been due largely to two factors, both of which arise from the high zinc content of the crusts from continuous desilverizing:

1. The large quantity of zinc distilling off during the operation results in a relatively small weight of retort bullion remaining in the bottle towards the conclusion of the operation when the highest temperature is reached.
2. The high zinc content of the crusts corresponds with a low specific gravity and as a result the bottle has a larger base less liable to crushing.

A large tilting retort furnace is used at Port Pirie. Silver-zinc alloy in the form of pellets weighing 5½ lb. is charged into the heated retort. When full of molten alloy the condenser is fastened in position and the junction of the condenser and furnace face luted with fire clay. Zinc distills over and liquefies in the condenser, which is tapped about every hour into a refractory-lined cast-iron conical bowl, then skimmed and cast into bars. These are returned to the desilverizing kettle. When distillation is complete, the condenser is removed and retort bullion, after removal of surface dross, is poured into a specially constructed ladle lined with firebrick. For pouring the bullion, the furnace-tilting gear is used.

The retort bullion is again skimmed in the ladle, then cast into bars and sent to the cupellation furnace.

All drosses are stacked in a bin and later treated as described below under "sweating."

A certain amount of blue powder forms in the condenser, which is raked out after each charge treatment. This is screened to separate lumps of zinc and the blue powder is sent to the roasting plant where its zinc content becomes absorbed in sinter, and eventually appears in the smelter slag.

Cupellation Section.—The cupellation furnace was designed to allow a high treatment rate to be obtained with a view to decreasing the cost of cupellation. This end has been achieved by the addition of "antimonial slag" to the cupel; the oxides of arsenic and antimony act as oxygen carriers in the cupel slag and result in a marked increase in the rate at which the bullion is oxidized.

The cupellation practice may be divided into three distinct operations: (1) sweating of retort and other rich drosses to recover their silver and gold contents directly followed in the same furnace by (2) concentration of the sweat lead and retort bullion to rough doré bullion, which is dipped into bars and charged to a clean furnace; (3) refining of the rough doré, giving a high-grade doré, which is dipped into plates for parting.

For treatment of drosses a bath of retort bullion is first made in the furnace and drossed; if very rich, the retort bullion is broken down with lead. Drosses are next charged in and a temperature of 900° to 1000° C. maintained in the furnace. Lead and zinc are oxidized and form a dry dross on the surface of the bath. "Antimonial slag" is added, forming a semifluid dross, which is hooked off into pots and returned to the blast furnaces. When the dross treatment is complete, the process of concentration continues in the same furnace.

To the sweat lead in the cupel is added retort bullion, and as before lead and zinc are oxidized, forming a fluid slag. At this stage, side air jets are turned on which blow over the slag surface, producing a rippling effect and exposing the metal beneath. These aid oxidation, which is further accelerated by the addition of antimonial slag. The slag formed is run off through a small water-cooled notch, the overflow level being carefully adjusted to prevent loss of metal. As oxidation and removal of slag proceed more retort bullion is added, until finally, when all slag has been carefully removed, a full furnace charge of doré remains. Slag from the process of concentrating likewise returns to the blast furnaces for re-treatment. The doré is dipped into rough bars and later refined in a clean furnace. Throughout the operation the temperature is gradually increased and at its conclusion reaches about 1100° C.

In the refining furnace the doré is remelted and a small quantity of crushed marble thrown on the surface and skimmed off. The purity of the charge is adjudged by the appearance of a sample of the metal allowed to solidify in a 3-in. dia. ladle. The refined metal is dipped into plates of 250 oz. weight of the average dimensions: 10¾ by 7½ by ¾ inches.

Since the processes of sweating and concentration are much more severe upon furnace brickwork than the refining process, the furnace in which the former operations are carried out always reaches the repair stage first. The practice has been adopted of reserving the new furnace for refining, the sweating and concentrating being then transferred to the furnace previously used for refining.

Before dipping is commenced, a sample is taken from the charge, poured into water and 4 oz. of granulated doré selected as an assay sample. After dipping every 80 plates (i.e., 20,000 oz.) a similar sample is taken from the furnaces. The following figures represent an average analysis of doré bullion over 12 weeks: Ag, 996 fine; Au, 19.15 oz. per ton; Cu, 0.21 per cent.

Doré Parting Plant.—The parting plant consists of 80 cells of the Balbach-Thum type. The cells are of glazed earthenware 1¼ in. thick. The cathode is formed by carbon slabs on the cell bottom. A wooden cradle covered with a canvas diaphragm contains the anode plates. The cradle is constructed so that sufficient clearance is allowed for the passage of a wooden scraper to rake out deposited silver.

The electrolyte is of the following approximate composition: Ag, 200 grams per liter; Cu, 25 to 30 grams per liter; HNO_3 (free), nil.

Silver is constantly being replenished by addition of concentrated silver nitrate solution prepared in an earthenware crock by dissolving doré plates in strong nitric acid. The nitrate is added to the cells by way of the cradle to avoid possible loss of gold. Concentration of silver is maintained at about 200 grams per liter to give a heavy granular type of cathode deposit and provide an electrolyte of high conductivity. If the concentration falls unduly, the cathode deposit tends to become bulky and "woolly," building up on the cathode plates and tending to cause short-circuiting. This involves much greater attention to cells.

Copper under normal conditions remains very constant at about the figure quoted, without other purification than (1) rejection of liquor from digestion of final or rich anode sludge with nitric acid, (2) removal from time to time of portion of the electrolyte in the cells treating "high-grade" doré which becomes enriched in copper.

High copper concentration (40 grams per liter or so) leads to trouble with canvas diaphragms, which tend to develop holes and cause excessive loss of gold.

Other elements are present in the electrolyte in very small amounts, chiefly lead and zinc. It was customary at one time to add to the cells a small quantity of ferric nitrate solution, which has a marked influence in promoting a granular type of cathode deposit. In the absence of free nitric acid, however, the iron cannot be held in solution, but the same end in regard to type of cathode silver is achieved by maintaining a fairly high silver concentration in the electrolyte as above described.

The electrolyte composition is checked once each week. A sample of 5 c.c. of electrolyte is taken from each cell and the samples bulked for each row of 20 cells, making four samples in all. Determinations are made of silver and copper only.

Deposited silver is raked forward in the cells every 4 hr., being drawn clear of the solution and allowed to drain upon the slope of the cell. The operator then draws beneath the line of cells a carriage holding a perforated aluminum tray, and sweeps the silver crystals into the tray by means of a short wide-bladed scraper. The cathode silver is washed on the tray with distilled water, the drainage liquor from the washing being used to replenish the electrolyte in the cells, to make up for losses due to evaporation and removal of solution in anode sludge.

The tray containing the washed silver crystals is discharged into a large steel drying tray. The latter is slid into a drying oven and when quite dry the silver is transferred to a storage bin to await final melting.

The dried cathode silver crystals are melted in a small reverberatory furnace, the silver being cast into market bars approximately 1100 oz. in weight, or granulated as required.

Anode sludge is allowed to accumulate in the canvas diaphragm for 25 days, then the cloth and contents are placed in a drying tray. A cycle of operations is arranged so that three cloths are changed each day, new cloths being placed in the cradles in their stead. The tray is placed in the drying oven, when the canvas burns off and leaves a dry flaky material, which every few days is melted down to yield a metal known as "high-grade" doré. A small amount of borax is used as a flux in melting and the slag formed returned to the cupels. The metal is cast into flat plates similar to the original doré plates, and again parted in a cell specially set aside for this purpose. The result is that a much enriched anode sludge is obtained for working up into the final gold bar.

Before melting, the sludge is digested with nitric acid, the liquor being rejected after precipitation of silver. The remaining gold is melted up with borax in a graphite pot in an oil-fired furnace. The bar from this is remelted with a little dehydrated borax and chlorine bubbled through it for refining. The final bar assays 997+ fineness.

Average analyses for the products of this section are:

	Market Silver		Refined Gold
Silver, per cent	99.97	Gold, per cent	99.7
Gold, oz. per ton	0.02		

Advantages of Continuous Refining Processes

The following is a brief discussion of the principal advantages of the continuous processes of lead refining over the old batch processes, which were previously employed at Port Pirie.

With regard to labor force, the advantages of the continuous processes are very striking. In the batch processes for softening and zinc refining, the operation involves the laborious skimming of dross by hand from the surface of the bullion bath, whereas in the continuous processes the dross runs from the furnace as a liquid slag, and little or no attention by the operator is required. Also, since in the continuous process a single unit replaces a large number of batch units, the duties of the operatives are simplified, being confined to one furnace, and the number of operations is correspondingly reduced.

Parkes desilverizing practice involves the skimming of the second silver zincing for return as first silver zincing to the next charge; however, the separation of the corresponding crusts takes place automatically in the continuous process in the cooler portion of the kettle, the crusts that separate rising on account of their lower specific gravity, and being partly dissolved in the incoming bullion and partly dissolved in the alloy layer.

The crusts finally dipped from the continuous desilverizing kettle contain only about 12 per cent lead, as compared with 75 to 80 per cent lead in those obtained in the Parkes process; hence, the quantity to be skimmed is correspondingly small—moreover, the operation of pressing is dispensed with. The relatively small quantity of crusts is responsible for a large reduction in the labor required for retorting and cupellation.

The batch processes of softening, desilverizing and zinc refining involve in their cycle of operations periods during which a peak load is placed on the operatives; since the labor force must be large enough to cope with the peak loads, there are periods between such peaks when the labor force is unnecessarily large. The continuous processes have the advantage that they involve no peak loads on the labor force, and hence the few operatives required are steadily employed.

A considerable saving in oil fuel results from the use of the continuous processes. This saving is particularly notable with continuous softening, where the combustion of lead, antimony and arsenic provides sufficient heat to maintain the furnace and its contents at the required temperature for the operation.

The repeated heating and cooling of batch units is partly responsible for high fuel consumption, but with a continuous unit the optimum temperature for the operation involved is continuously maintained, and a further saving of fuel results. The quantity of oil used in retorting and cupellation is reduced on account of the very small quantity of high-grade crusts treated.

The area occupied by the present refinery at Port Pirie is about one-third of that occupied by the old batch refinery, which it replaced. When all units in the latter refinery were in operation, it had a maximum capacity of 560 tons per day; it is estimated that with all units of the continuous refinery in operation a capacity of 1500 tons per day could be maintained. Operating only one unit in each section, the continuous refinery has produced over 16,000 tons of lead in a four-weeks period; that is to say, an average production of over 750 tons per day. This large reserve capacity renders the operation of the refinery exceedingly flexible, for whereas in a batch refinery if production is to be increased or decreased temporarily it is necessary to alter the number of units operating, with the continuous process it is simply a matter of adjusting the valve on the pump feeding the continuous softener furnace.

The flexibility is particularly valuable when, owing to variation in blast-furnace smelting speeds, the quantity of bullion supplied to the refinery is irregular, as the refinery flow can be speeded up or slowed down at will, without any alteration in the number of units operating.

The small size of the refinery means small construction and maintenance costs, and close technical control is achieved to a high degree.

The metallurgical advantages accruing from the employment of the continuous processes are of considerable moment. In the operation of the Parkes desilverizing process, the determination of the weight of zinc, which theoretically should be added to each charge for lowest zinc consumption, is difficult and complicated, and depends on such factors as: (1) desilverizing procedure, (2) silver content of bullion to be desilverized, (3) weight of bullion treated in each charge, (4) efficiency of separation of crusts from mother liquor.

In the continuous process, the quantity of zinc added to a definite quantity of bullion treated is not predetermined; the zinc layer gradually enriches in silver until it is removed from the kettle, and thus variations in such factors as treatment rate or silver content of the bullion to be desilverized are reflected only in the frequency of dipping, and do not influence the zinc consumption, which is thus always at a minimum.

When softening of bullion is being conducted according to batch practice, the presence of large quantities of arsenic and antimony renders the softening process longer, and consequently more costly; however, in the continuous softening process, a high arsenic and antimony content in the bullion becomes an advantage, since the make of slag in the softener

TABLE 1.—*Refinery Cost Factors*

FOR PRODUCTION AT RATE OF 4 TO 10 SHORT TONS PER HOUR[a]

LEAD REFINING

	Labor, Men per Shift	Oil, Gal. per Ton M. L.	Power, Kw-hr. per Ton M. L.	Coal, Lb. per Ton M. L.	Zinc, Lb. per Ton M. L.	Maintenance Labor, Man-days per 1000 Tons Lead	Maintenance Material, per 1000 Tons Market Lead							Compressed Air, Cu. Ft. Free Air per Min.	Salt Water, Gal. per Min.
							Chamotte, Lb.	Bricks. No.[b]	Castings, Lb.	Steel, Lb.	Agitators, Lb.[b]	Molds, No.	Pumps, Lb.		
Bullion storage and delivery to softeners		0.45	0.6			3.74	264		25				0.3 cast iron 0.6 steel		
Softening	0.5	0.36	0.12			8.42	106	126(s)		26	34 (pipe) 0.7 (st.)			150	95
Slag enrichment	0.5	0.36	0.4	6.8		1.17	160	38(s)	29		8 (pipe) 0.2 (st.)			75	80
Lead conditioning		0.45				0.70	53	27(s)							20
Desilverizing	2.0	1.00	1.0		13.5	9.36		168 (fb sil.)	1710						43
Refining	1.0	0.90	0.2			4.68	53	135(s)		26	22 (pipe) 0.5 (st.)			75	85
Market-lead storage and dross dump	1.0	0.18	0.2						32						
Molding, weighing and delivery to stock	4.0		0.8			9.83						1.0	Pence per ton 0.3 (trucks and elec. gear)		
Lead-refining totals	9.0	3.70	3.32	6.8	13.5	37.90								300	323

SILVER REFINING

	Labor, Man-days per 1000 Oz. Ag	Oil, Gal. per 1000 Oz. Ag	Power, Kw-hr. per 1000 Oz. Ag	Maintenance, Man-days per 1000 Oz. Ag	Maintenance Material per 1000 Ounces Silver			Salt Water, Gals. per Min.
					Bricks, No.	Steel, Lb.	Retorts	
Retorting	0.231	23.2	6.2	0.0624	0.05 sil. 0.0015 carbolox	0.003	One per 190,000 oz.	
Cupellation, including sweating of drosses	0.105	10.2	3.1	0.0208	0.013 chrome 0.037 alumina	0.003		40
Doré parting	0.170	0.9	35.0					20
Melting cathode silver	0.022	1.5	0.5					
Drossing and weighing silver	0.084							
Treatment and weighing gold	0.011							
Silver-refining totals	0.623	35.8						60

[a] Short tons and British imperial gallons used throughout.

[b] (s), steatite; fb, firebrick; sil., silica brick; st., stainless steel.

furnace is increased, and consequently the greater heat of formation of lead, antimony and arsenic oxides ensures ample heat for operation of the furnace, without the use of extraneous fuel; and, secondly, a smaller proportion of the total lead has to pass through the desilverizing kettle, the remainder flowing directly to the zinc-refining furnace from the antimony-dross furnace in the form of hard lead, with consequent reduction in zinc consumption.

The increased efficiency of desilverizing by the continuous process results in the recovery of an extra 0.1 to 0.2 oz. of silver per ton of bullion treated.

The quantity of metal lost in flue gases from the continuous refinery is so small that attempts at recovery of fume by any of the standard methods are not at present considered justifiable; however, the volume of waste gases is very low, and would readily permit the installation of a small unit for recovery of metal values.

The fact that all litharges or drosses from softening and refining are handled in a molten state eliminates the dusty nature of the old process of skimming a furnace, thus reducing the risk of industrial disease.

A further advantage of the continuous processes is the small quantity of lead and silver incirculation; the total lead incirculation in the Port Pirie refinery is one day's production, and the whole of this lead is immediately recoverable.

Maintenance costs in the continuous refinery are low because of the excellent operating life of the various units. The use of steatite bricks in the softener, temperature-control, zinc-refining and antimony-dross furnaces has proved highly successful. The life of the top arch and side walls of the softener and zinc-refining furnaces and of the top and cone castings of the desilverizing kettles is approximately three months, so that they each serve for the treatment of about 40,000 tons of bullion.

The antimony-dross and temperature-control furnaces and the straight and bottom sections of the desilverizing kettles require renewal after a year and a half to two years continuous operation, while the life of the bottom of the softener and zinc-refining furnaces is about six months.

In order to illustrate the effect of the advantages of the continuous process on the cost of refining drossed smelter bullion, the schedule of costs in Table 1 is included. This schedule is referable to flows of 4 to 10 tons per hour, and should thus be of more general interest than figures for the normal Port Pirie flow of about 20 tons per hour.

CONSTRUCTION DETAILS

This section gives a description of the details of construction of the various units of the continuous refinery. The bullion-storage kettles and molding section have not been included because their mode of construction follows established practice.

Softening Furnace

Furnace Dimensions.—The furnace occupies an area of 6 ft. 6 in. by 16 ft. 6 in. external with 75 sq. ft. hearth area over the invert (Fig. 5). The thickness of hearth at the lowest point of the invert is 15½ in., the hearth having a 3½-in. dish to center. The walls and top arch are 9 in. thick. The height from center of hearth surface to lead notch is 11½ in., the slag overflow being 2½ in. higher. From slag overflow to spring of top arch is 28½ in., the arch rising 3½ in. to the center.

Furnace Supports.—The furnace is supported by 6 by 3-in. R.S. joists at 20-in. centers providing free air space beneath the furnace.

Hearth.—The hearth is of 9-in. brick on a concrete bed of minimum thickness 6½ in. The invert is dished 3½ in. to the center of the hearth.

The concrete mix used for the bed is four parts lead blast-furnace slag, ¾ in.; two parts siliceous sand, ¼ in.; one part standard Portland cement by volume.

Crucible Tank.—The furnace is built in a steel tank 30½ in. deep, of welded construction throughout, with side of ⅜-in. M.S. plate and bottom ½-in. M.S. plate.

Brickwork.—Bricks and blocks throughout are of steatite, prepared by crushing selected quarried steatite, bonding with silicate of soda, molding and burning. Brickwork is jointed with a mixture of crushed steatite and silicate of soda. For the lining and the main jackets bricks are used and cut to the required shape, the brickwork being carried by steel angles welded to buckstays. As an insulating cover outside the slag jacket, chamotte (four parts finely crushed burned fire clay to one part of Portland cement) is used. The mixture is held in position by a steel apron plate.

Water Jackets.—Side walls are jacketed for a height of 20 in. above the hearth, the jackets being of special shape shown, with four sections on each side, two on the end distant from the lead and slag notches, and special jackets as shown at the discharge end. Water-cooled plates are set over the top arch, and are used as an operating platform, the upper surface being of checker plate. For cooling water supply, a 6-in. pipe is set around the furnace with a 6-in. inlet from the main service. All jacket sections are connected in series from the 6-in. main by 1¼-in. dia. pipes, except in the slag spout, where ¾-in. connections are used. Flexible connections are necessary.

Total consumption under operating conditions is 8000 gal. salt water per hour. All jackets are manufactured from 3⁄16 in. thick M.S. plate, open-hearth steel, the jackets being of welded construction throughout.

Lead Inlet.—Submerged flow into the furnace is obtained by the use of an external lead well situated on the side of the furnace.

Lead Outlet.—The lead outlet comprises a jacket with an overflow notch behind, which is a special D-shaped jacket forming in effect a lead well within the furnace, and giving a submerged outflow of bullion from the bath.

Slag Outlet.—For the slag outlet, a jacket with a notch 3 in. wide and 5 in. deep is employed; a water-cooled slag launder is attached below the notch.

Buckstays.—Buckstays must be welded to tank.

Firing.—Furnace is oil-fired from the end distant from the lead and slag outlets by means of a burner with maximum capacity of 12 gal. oil per hour.

Agitators.—The number and size of the agitators used vary. Holes 6 in. in diameter are provided in the four center top arch jackets. The agitators consist of a steel pipe terminating in a stainless-steel cylindrical block with several holes drilled diametrically for air discharge. The pipe is connected to the compressed-air service (pressure 90 lb. per sq. in.) and water-jacketed by means of two steel pipes set concentrically around the air pipe, the salt water passing down the inner pipe and rising in the annular space between the inner and outer pipes. The size of the central air pipe is 1 in., ¾ in. or ⅜ in., according to the size of the agitator. The larger sizes are normally used in the softener furnace.

Antimony-dross Furnace

The antimony-dross furnace (Fig. 6) is built in a rectangular stee tank, 16 ft. 6 in. by 13 ft. 5 in. by 30 in. deep, which is supported on 6 by 3-in. R.S. joists not more than 21 in. apart. The hearth, which has the form of an inverted arch with an area in plan of 168 sq. ft., has a minimuml thickness of 15 in. The maximum depth of the metal bath is 11½ in. below the lead outlet, the slag outlet being 2½ in. higher.

Combustion space is a constant height, 2 ft. 4 in. at the sides and 3 ft. at the center above the slag level, throughout the length of the furnace.

Hearth.—The hearth is of brick, 9 in. in the center and 14 in. near the sides, set in a concrete bed formed to the shape with a minimum thickness of 6 in. Depth of invert at the center is 6 inches.

Crucible Tank.—The tank is of M.S. welded plate, ½ in. thick on the bottom and ⅜ in. on the sides, stiffened with angle irons.

Brickwork.—All brickwork is of steatite brick, as specified for the softener.

Water Jackets.—Water jackets are installed around the metal bath only, and are made of 6-in. dia. pipe flattened to 8¾ and 2⅝ in. section. The quantity of water used in these jackets under normal operating conditions is 12,000 gal. per hour.

Five sections of water-cooled plate are set on the top arch, openings being provided for three agitators, and one for charging antimony dross.

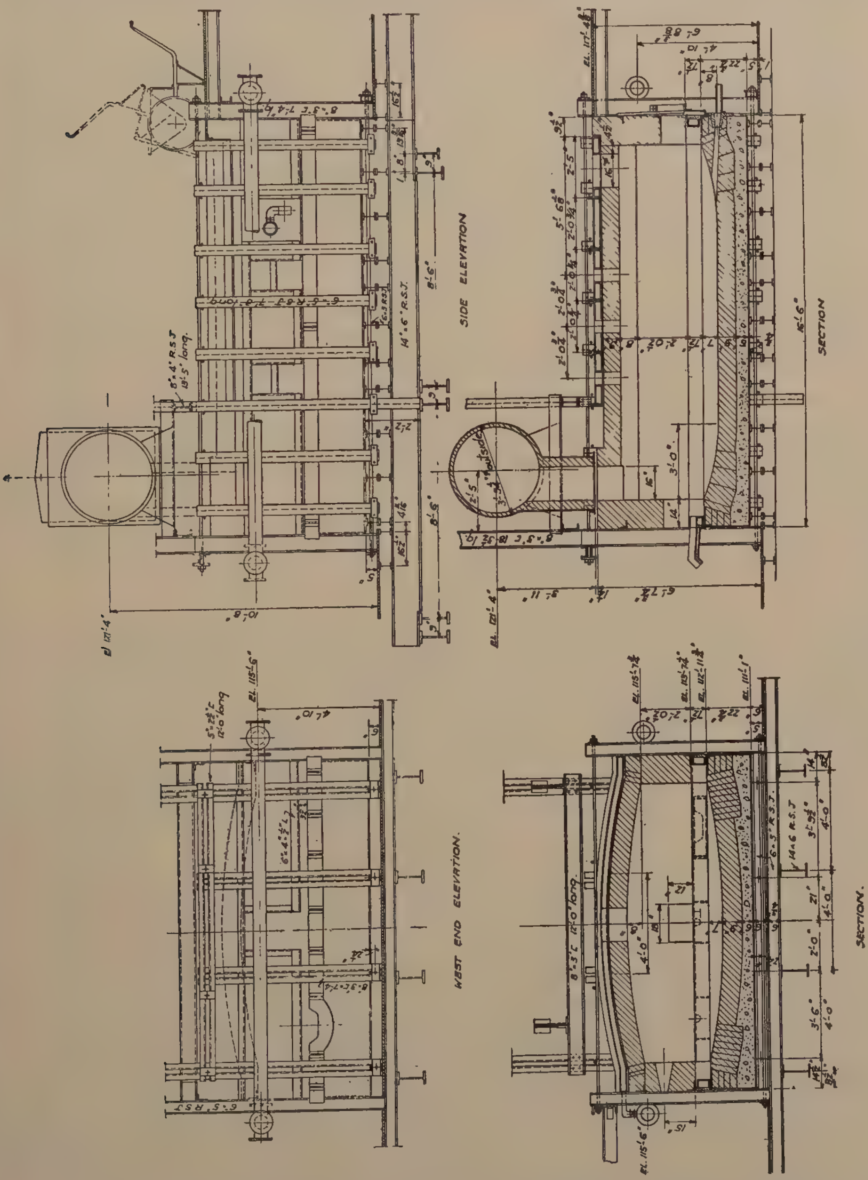


FIG. 6.—ANTIMONY-DROSS FURNACE.

Inlets and Outlets.—The furnace is charged through a 16-in. dia. opening in the top arch situated in the center of the arch at the end distant from the flue.

The usual combination of D-jacket and overflow notch is provided for the hard-lead outlet. The slag outlet is a notch 3 by 3 in. in a section of the flattened pipe jacket. The welds at the notch are protected by steatite.

Both outlets are at the flue end of the furnace, on opposite sides of the furnace center line. The slag notch has a short water-cooled launder. A skimming door 18 by 12 in. deep is situated between the slag and lead outlets and is covered by a steel plate.

Buckstays, Tie Rods, Etc.—Buckstays are 6 by 5-in. R.S.J.'s, welded to the tank, and are each cross connected at both top and bottom by 1-in. dia. tie rods. The maximum distance between buckstays is 2 ft. 5 in. On the ends are four sets of buckstays each 8 by 3-in. channels connected by 1-in. dia. tie rods. The thrust of the top arches is taken by 4 by 4 by ½-in. angles.

Top Arch and Side Walls.—The top arch is of 9-in. brickwork, rising 8 in. to the center of the arch, with a 16 by 24-in. inlet for slag, and three 6-in. dia. holes for agitators. Side walls are of 14-in. brickwork.

Firing.—The furnace is oil-fired by a burner capable of burning a maximum of 24 gal. of oil per hour, through the side wall 4 ft. 6 in. from the charging end.

Agitators.—As specified for the softener furnace, the smallest size with ⅜-in. dia. compressed-air pipe.

Temperature-control Furnace

The temperature-control furnace is constructed in a rectangular steel tank 6 ft. 6 in. by 16 ft. 6 in. by 2 ft. 6 in. deep, supported above the floor by steel joists (6 by 3-in. R.S.J.'s at 21-in. centers). The hearth has an area of 75 sq. ft. with a minimum thickness of 19 in. on its longitudinal center line, the surface rising with inverted arch formation to a height of 3½ in. to the side and end walls. The walls and top arch are of 9-in. brickwork.

The depth of the metal bath is 7½ in. The inlet and outlet notches are at the same level.

Combustion space above the bath is 2 ft. 4 in. high to the spring of the top arch at the inlet or flue end dropping 1 ft. 4 in. at the outlet or firing end. The rise of the arch is 3½ in. to center. The offtake flue is 14 by 24-in. section. An opening 8 by 32 in. is provided in the side wall near the softened-bullion inlet end for the skimming of dross from the furnace and an opening 12 in. square on the same wall for inspection.

Hearth.—The hearth is of 9-in. brick on concrete bed formed to the hearth shape with a minimum thickness of 10 inches.

Crucible Tank.—The crucible tank is of M.S. plate ½ in. thick on the bottom and ⅜ in. at the sides, suitably stiffened with angle irons and of all-welded construction.

Brickwork.—All brickwork is of steatite to the specification given for the softening furnace, except for the lining to water jackets around the metal bath, where chamotte is used.

Water Jackets.—Jackets are used only around the metal bath and are manufactured from 6-in. dia. piping flattened to 8¾ by 2⅜-in. section. Inlet and outlet notches are 6 by 5 in. deep with the jacket section compensated. The tops of the jackets project 1½ in. above the top of the tank. There are separate jackets for inlet and outlet and two sections on each side. The jackets on each side are connected in series.

Buckstays, Tie Rods, Etc.—Buckstays, which consist of two 5 by 2½-in. channels, are spaced not more than 3 ft. 7 in. apart at the sides. On the ends are two sets of buckstays 5 ft. 3½ in. apart. All buckstays are welded to the tank, and coupled top and bottom across the furnace by 1-in. dia. tie rods. Skewback angles 4 by 4 by ½ in. are welded to buckstays to take thrust of top arch.

Top Arch.—The top arch is of 9-in. brick rising 3½ in. to center.

Firing.—The furnace is fired by a burner capable of burning up to 12 gal. of oil per hour, located in the end wall above the outlet, the products of combustion being carried off by a flue at the bullion-inlet end.

Desilverizing Kettle

The desilverizing kettle (Fig. 7) is of cast iron divided into four sections, connected by special joins, the bottom section bearing directly on a heavy reinforced concrete foundation, the whole enclosed in brickwork (Fig. 8) built to form six firing hearths around the kettle, three for the bottom section, and one each for the other sections, the brickwork being tied by steel members. The maximum diameter of the kettle is 10 ft. internally and the over-all height of the casting is 23 feet.

Standard firebricks are used throughout except for baffle walls in the top firing chamber where silica bricks are used. All bricks are clay jointed. The setting (Fig. 8) consists of brick walls 9 in. thick constructed to form a rectangle 13 ft. 10 in. by 16 ft. 4 in. with divisions spanning the area between the walls and the kettle, dividing the space into a tier of six combustion chambers with intermediate pockets around kettle flanges. The divisions are supported at their outer extremities by the brick walls, and at their inner by the flanges or walls of the kettle. Where divisions abut to the cast-iron kettle, brickwork is arched between the 13-ft. 10-in. walls, except the top arch, which spans between the 16-ft. 4-in. walls. Tiles are used for the divisions, which rest on flanges.

Each of the six combustion chambers has two burners, both affixed to the same wall—one right and one left of the kettle center line—with flue outlet between the longitudinal baffle walls directing gases around the kettle, preventing short-circuiting to the flue. Each burner on all chambers is suitable for the combustion of 12 gal. of oil per hour maximum.

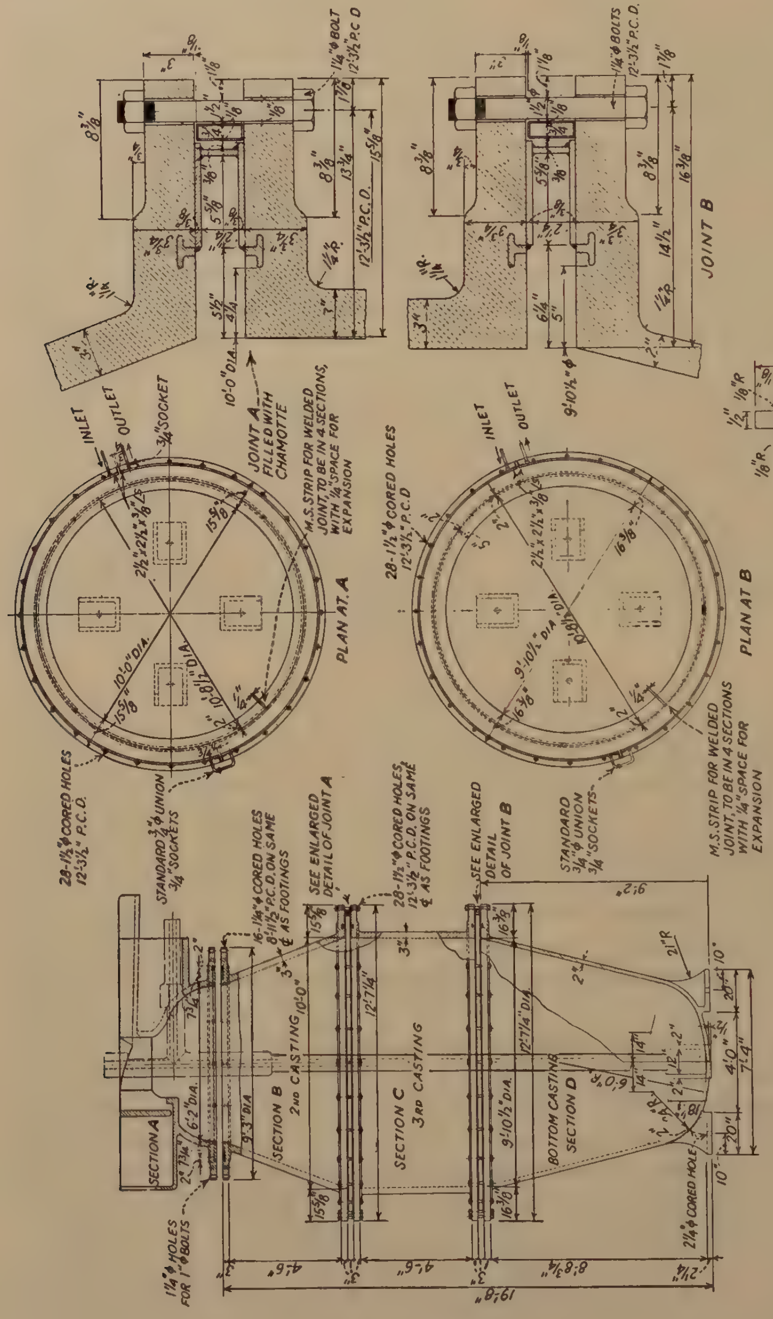


FIG. 7.—DETAILS OF DESILVERIZING KETTLE.

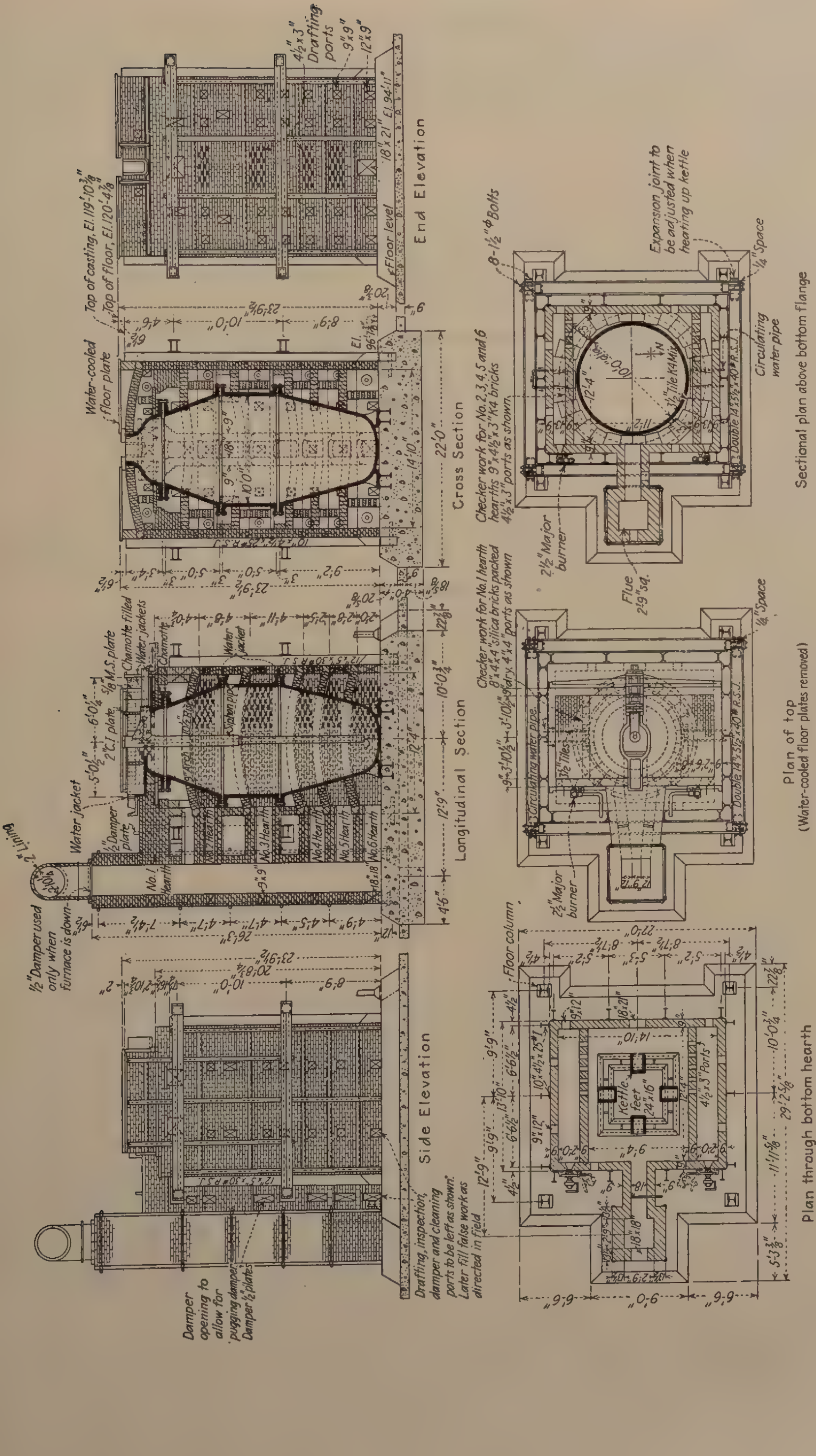

End Elevation
Cross Section
Longitudinal Section
Side Elevation
Plan through bottom hearth
Plan of top
(Water-cooled floor plates removed)
Sectional plan above bottom flange
4½"x3" Drafting ports
9"x9"
12"x9"
Top of casting, El. 119'-10⅜"
Top of Floor, El. 120'-4⅛"
Floor level
18"x21" El. 94'-11"
Water-cooled floor plate
El. 96'-7⅜"
22'-0"
14'-10"
10'-0"
23'-9½"
½" Damper used only when furnace is down
2" Lining
Water jacket
½" Damper plate
Chamotte filled Water jackets
⅝" M.S. plate
2" C.I. plate
Chamotte
Water jacket
No. 1 Hearth
No. 2 Hearth
No. 3 Hearth
No. 4 Hearth
No. 5 Hearth
No. 6 Hearth
26'-3"
12'-9"
10'-0¼"
4'-6"
Damper opening to allow for pugging damper. Damper ½" plates
Drafting, inspection, damper and cleaning ports to be left as shown. Later fill false work as directed in field
Floor column
Checker work for No. 2, 3, 4, 5 and 6 hearths 9"x4½"x3" K4 bricks 4½"x3" ports as shown
Checker work for No. 1 hearth 8"x4"x4" silica bricks packed dry. 4"x4" ports as shown
8-1½" ϕ Bolts
Expansion joint to be adjusted when heating up kettle
¼" Space
Circulating water pipe
Double 14"x5½"x40# R.S.J.
3½" Tile K4 Mix
2½" Major burner
Flue 2'9" sq.
Kettle feet 24"x16"
4½"x3" Ports
22'-0"
9'-9"
9'-0"

FIG. 8.—SETTING FOR SILVER KETTLE.

The top chamber is divided into two compartments, each with separate outlet to flue 12 in. wide. Other chambers have each one outlet to the flue 18 in. wide. Ports are left and filled with loose bricks in outer walls at all vantage points for inspection and air intake as required.

Buckstays.—R.S.J.'s 12 by 5 in. are used at 5-ft. 2-in. centers against the walls that take the lower arch thrusts, and 10 by 4½-in. R.S.J.'s against the 16-ft. 4-in. walls opposing the top arch thrust. Thrust angles 4 by 4 by ½ in. are used except at the top, where the size is increased to 6 by 4 by ½ in., all angles being bolted to overhead buckstays supported by a horizontal double band of 14 by 5½-in. R.S.J.'s at the top, with a similar double row of 14 by 2½-in. R.S.J.'s 8 ft. 9 in. above foundation. Joists are linked at the corners by adjustable connections to provide for expansion.

Flues.—The main flue is vertical 2 ft. 9 in. square internally with 13½-in. walls with separate connections for each chamber.

Castings.—Metal is 3 in. thick throughout for kettle castings except for: (1) walls of bottom section, which are 2 in., (2) thickening due to fillets at junction of flanges and kettle shell.

The top casting is of special section with an inlet box that is a separate casting forming a trap to prevent ingress of dross and giving a submerged intake. Desilverized lead is discharged from the kettle through a siphon pipe, provision being made in the casting to take the delivery arm of the pipe, which is held in position by vertical plates studded to the casting, leaking from the upper portion of the kettle being prevented by luting between plates and around the pipe with chamotte, the holding down plates and packing being fixed on the outer vertical surface by a water jacket.

The siphon pipe is of cast iron with a 3½-in. diameter bore throughout, the thickness of metal in the upper section being 4 in. reduced to 2 in. for the lower portion.

A 1¼-in. dia. rod is passed through the pipe and has a 2-in. square return welded to the bottom end.

Joints.—Castings are jointed by casting M.S. tee rings 2 by 1⅛ in. in flanges and welding thereto M.S. flats ⅜ in. thick, as shown, to form a flexible joint, the distance between flanges being 3 in., the space being packed with chamotte.

A water jacket 2⅝ by ¾ in. internal in two semicircular sections is used in addition for the lower joints only, the sections for each ring being connected in series, the inlets and outlets being ¾-in. dia. A third jacket is carried around over the heads of the bolts of the top joint, the halves having ¾-in. connections in parallel.

Fresh water (1000 gal. per hour) is used for circulating through the jackets.

Floor Plates.—The working area around the top of the kettle and covering the setting is floored with hollow steel plates from 3⁄16-in. steel. Water is circulated through the plates, each section having a 1-in. dia. inlet with outlet diagonally opposite. Cooling water used amounts to 2000 gal. per hour.

Zinc-refining Furnace

The zinc-refining furnace is set in a rectangular steel tank 6 ft. 6 in. by 16 ft. 6 in. by 3 ft. 3½ in. deep, with its bottom supported above the floor by 8 by 4-in. R.S. joists at 21-in. centers. The hearth is 15 sq. ft. in area and 16½ in. thick at the thinnest section—the center of the inverted arch formed between the side walls. The arch drops 4 in. from side walls to center. Walls and top arch are of 9-in. brickwork.

The depth of metal below the lead outlet is 18 in., the slag overflow being 1½ in. higher.

Combustion space is 2 ft. 9½ in. above slag level at the firing end, diminishing to 15½ in. at the flue offtake end, both measurements being to spring of top arch at side walls and increase 3 in. to the center.

The flue offtake is 3 ft. 6 in. by 14 in.

Hearth.—The hearth is of 9-in. brick set in a concrete bed formed to the shape of the hearth with a minimum thickness of 7½ in. A small channel is built in the hearth at one end, connecting to a drain pipe consisting of a C.I. breast and spout, the breast opening increasing from 1¾-in. dia. to 3-in. dia. at the outside.

Crucible Tank.—The tank is of welded M.S. plate ½ in. thick on the bottom and ⅜ in. thick on the sides. Holes 1-in. dia. are drilled in the tank for drainage.

Brickwork.—All brickwork is of steatite bricks, as described for the softener furnace.

Water Jackets.—Jackets around the metal bath are of similar construction to those on the temperature-control furnace, except at the lead and slag outlets, where special sections as described for the softener furnace are employed. Jackets are welded from mild-steel plate 3⁄16 in. thick, and all welds over which metal and slag flow are protected by stellite ⅛ in. thick.

Each jacket section has a direct valve-controlled connection from the 6-in. supply main around the furnace, 1-in. dia. in squash jackets and 1½-in. dia. for outlet notches, with direct connection of similar size to drain, all jackets parallel connected. Flow of cooling water through the jackets around the metal bath averages, including notches, 8000 gal. per hour.

The top arch is also covered by water jackets having a 3-in. water space, 1½-in. supply and drain connections in parallel, inlet and outlet for each section being at diagonally opposite corners. Six sections cover the full length of the furnace, openings being provided in four for the admission of agitators, and in one for the desilverized lead inlet. Jacket construction is of ¼-in. M.S. plate welded. The top plates are 5⁄16 in. thick with checkered surface. Water used for roof jackets amounts to 2000 gal. per hour.

Inlets and Outlets.—Molten lead is charged through a 6-in. dia. opening in the top arch, situated with the center line of the hole 18 in. from the side wall and 8 ft. 8 in. from the outlet end wall. The lead outlet is at the flue end with the slag notch in the adjacent side. The slag runs down a sloping launder of water-jacket construction.

Buckstays, Tie Rods, Etc.—Brickwork is tied by steel buckstays at not greater than 3-ft. centers, each consisting of two 6 by 3-in. channels welded to the crucible tank and connected top and bottom across the furnace by 1-in. tie rods.

Top Arch.—The top arch is of 9-in. brick with a 3-in. rise to its center and covered by water jackets, as previously described.

Firing.—The furnace is oil-fired by means of a burner installed on the end opposite the flue offtake, which is capable of burning 24 gal. per hour maximum.

Agitators.—Agitators of the type described in connection with the softener furnace are employed. Those used in the zinc refiner have a central air pipe ⅜ in. in diameter.

Charging Antimonial Slag.—Slag is charged through the roof by means of a chute situated on the furnace center line, at the extreme end opposite the flue. The flow is controlled by a slowly moving conveyor belt, the speed of which can be readily adjusted.

Retorting Furnaces

The plant consists of four furnaces on a common center line, outer center distances being 13 ft. 6 in. and space between furnaces 11 ft. 0 inches.

Furnace casing is of 1-in. cast-steel plate connected at corners by angle irons and bolted together. The side plates are flanged at the bottom, to give a landing for 45-lb. section rails, on which the bottom cast-iron plate rests.

The furnace is built of 9-in. thick special silica brick with the exception of the bottle seating, which is of Carbolox brick (carborundum refractory).

Flue offtake measuring 18 by 12 in. is horizontal on top of and built integral with retort brickwork, with a 12 by 8-in. opening from combustion chamber above neck of bottle. With the furnace in the vertical position, the discharge opening at rear of gas offtake comes to rest against the mouth of the branch from 18-in. dia. downcomer from main flue, a vertical counterpassed C.I. damper being installed in each branch. Downcomer and branch are mild steel cased with 3-in. firebrick lining.

Retort bottles A.P. (Q-80) Salamander crucibles from Morgan Crucible Co. are supported in an inclined position at the neck by front plate and lining, at the rear by the split seat of Carbolox bricks through which a 3½-in. Major rotary oil-burner fires. (Maximum capacity of burner is 24 gal. per hour.) Retort bottle is 12¾-in. dia. at the top, 34-in. dia. at the bulge and 24-in. dia. at the bottom, with a height of 50½ in., all outside measurements. The walls are 1½ in. thick at top to 3 in. at bottom, with bottom thickness of 2⅜ in. Bottle weighs 5 cwt. 1 qr. empty, has a flush capacity of 11.33 cu. ft. and in the inclined operating conditions will take an average of 37 cwt. (4100 lb.).

Condensers fitted to the mouths of crucibles are of M.S. ¼ in. thick plate lined with 1½-in. refractory of 12.5 per cent clay, 37.5 per cent sand and 50 per cent cement, 2-ft. 6-in. dia. by 4 ft. 0 in. long extended and reduced at mouth to match bottle to which condenser is luted. Condensers are supported by slinging from a 2-ton chain block carried by a 3-ft. 4½-in. radius jib arm having a 2½-in. dia. center post bracketed from 10 by 8-in. R.S. joist column and turning in S.K.F. T-16 thrust bearings. Jib is of two 3 by 2½ by ⅜-in. angles with 1½-in. dia. tie rod.

Trunnions are fitted in the center of the furnace side plates and rest in 3½-in. bearings fitted with C.R.M. 28 S.K.F. rollers, the whole furnace being carried on these bearings, one each side on cast brackets bolted down to the concrete foundation.

Block attachment to side plate with threaded screw and hand wheel provide the means for tilting furnace, which can be thus moved through an angle of 45° in the vertical plane.

Cupellation Furnaces

There are two cupellation furnaces. Refractory work is of alumina brick throughout. Brickwork for invert and walls is 9 in. thick with top arch 4½ in. thick.

Water jacket around the bath consists of a 1¼-in. dia. pipe bedded in a barites and cement mixture.

Crucible tanks are of steel with bottoms ½ in. thick, sides ⅜ in. thick, each measuring 10 ft. 6 in. by 3 ft. 0 in. by 16½ in. deep, stiffened by four 4 by 3 by ½-in. angles on the under side. Corner buckstays are of double-section 5 by 2½-in. channels, welded to tank, and extend to ground level acting as supporting legs for furnace, there being a 20-in. space from floor to bottom of crucible. Intermediate buckstays are of 4 by 4 by ½-in. angles. Skewback angles supporting the top arch are 4 by 4 by ½ inches.

Furnace is oil-fired by a burner of maximum capacity, 24 gal. per hour. The flue offtake, 18 by 9 in., is through arch at opposite end, each offtake connecting to a common header 1 ft. 9 in. internal diameter connecting to main flue. Header and flue connections are steel cased by ⅛-in. thick plate with 3-in. brick lining.

Electrolytic Parting Plant

The parting plant consists of 80 cells in four groups of 20 cells each, the groups being connected in parallel and the cells within each group in series. For each group of 20 cells, there is an instrument panel containing a main isolating switch, ammeter, low-range voltmeter and plug sockets for determining the voltage drop across every cell individually.

Cells are placed with 3-in. air space between them, and each cell rests on four porcelain insulators capped with acid-resisting rubber pads. Height from floor to top of cells is 3 ft. 3 in. Cell tables are built up of brick, the table surface and side of the upper course being of white glazed tile, while the top slopes ½ in. to center channel, which falls ½ in. from each end to center, connecting there to a vertical 2-in. earthenware pipe to drain below. Drains and cable ducts are ½-in. C.I. plates.

Cells are of glazed earthenware 1¼ in. thick, one end being vertical and the other (the front of the cell) having the form of a sloping lip. A wooden cradle to take the anode plates rests against the back of the cell, and sufficient clearance remains at the front to enable a wooden scraper to be pushed under the cradle and deposited silver to be raked forward onto the front slope of the cell.

Cradles are of oregon and the cross-bearers to carry the anode plates are of 1 1/16-in. O.D. boiler-gauge glasses. These are so fitted as to be easily removed. Inside the cradle rests the diaphragm of 15-oz. per yard canvas duck, previously washed to remove the dressing. This is stretched taut by a closely fitting timber frame pressed inside the cradle. The inner frames are of celery-top pine, oregon having been found unsuitable.

The anode plates rest on the diaphragm—four plates per cell—and across the junctions between the plates is set a contact piece (also of doré) connecting to the anode leads by means of a brass collar (i.e., two anodic contacts per cell).

Cathodes are Acheson carbon slabs, covering the whole of the horizontal cell bottom. On one side of the cell is a carbon lead-up plate resting against the main cathode surface. The other end is connected by copper clip to the cathode lead. This passes down and through the brickwork table to a bus bar on the opposite side.

Anode and cathode connections to bus bar are separated by a knife switch, normally open but closed to isolate the cell by short-circuiting.

Clearance between lower-surface anode plates and cathode surface is 3½ to 4 inches.

For the generation of direct current of the necessary amperage and pressure, two machines are installed in a specially constructed room, one of the two being a reserve set.

Each machine consists of a 550-amp. 60 to 125-volt self-excited shunt-wound compole screen-protected British Thompson Houston direct-current generator, 960 r.p.m. with frame D.S. 11W and two end shield journal bearings coupled to 75-hp. 960-r.p.m. protected General Electric motor, the whole being mounted on a combination steel bedplate 83⅜ in. long by 39 in. wide by 9¼ in. high.

For controlling fields of generators, shunt field rheostats were installed, operated by single-phase a.c. 50-cycle 550-volt motors. The 75-hp. motors were fitted with compensator-type C.R. 1034 starters.

Chlorine Dezincing in Lead Refining

By Jesse O. Betterton,* Maurer, N. J.

(New York Meeting, February, 1933)

In the Parkes process of lead refining, after desilverization has been completed by means of zinc additions, there will remain in the lead from 0.5 to 0.6 per cent zinc. At this stage in the refining practically all impurities are reduced to refined lead specifications except zinc and antimony. All excess of copper and nearly all the arsenic goes out with the silver. Silver remaining should not exceed 0.1 oz. per ton. It thus remains only to remove zinc and antimony to produce refined lead.

The older practice was to complete refining by means of oxidation processes in reverberatory furnaces. Essentially this consisted of heating the lead to 1200° to 1300° F. and allowing it to come in contact with a considerable excess of air passing through the furnace, or accomplish the same result by blowing the lead with steam by means of pipes introduced for that purpose, at the same time allowing air to enter the furnace. Usually some procedure involving alternate oxidation and reduction with fine coal or coke was employed in order to reduce the weight of dross or skim finally removed from the furnace.

This practice had many elements of weakness in that the main flow of lead, after the preceding expensive operations had been performed, and the whole refining process nearly completed, was subjected to an operation at a comparatively high temperature, which involved much lead loss if the furnaces were not on bags, and the production of 3 to 5 per cent of the weight of the lead as dross or skim, which had to be resmelted and the lead either refined or produced as antimonial lead. In addition, the operating expense of the process was a considerable item.

The process of dezincing with chlorine was developed as a substitute for the foregoing described oxidation process, and finally resulted in such advantages as nearly equal operating costs, a practical elimination of the lead loss, and the direct production of a very valuable byproduct, zinc chloride, that may be sold as such or retreated for its zinc and chlorine contents, both of which can be reused in the refining processes.

Essentially this process consists of circulating the lead by means of a pump in a kettle through a closed reaction cylinder, gaseous chlorine entering the reaction cylinder with the stream of lead from the pump. Molten zinc chloride is thus produced and is discharged together with

---

Manuscript received at the office of the Institute Jan. 15, 1933.

* General Manager of Lead Refineries, American Smelting & Refining Co.

the lead from the reaction cylinder and floats on top of the mass of lead in the kettle. The zinc chloride is removed from the lead by skimming, remelted, and treated with zinc to free it of both metallics and combined lead, and packed as a commercial zinc chloride for various uses.

The process is rapid and simple, conducted at moderate temperatures, 660° to 750° F., can be applied with ordinary and fully dependable equipment, and is free from noxious chlorine fumes to a surprising degree. Very little, if any, fuel is required as the reaction is markedly exothermic.

Equipment and Its Uses

Dezincing Machine.—The equipment employed in this operation consists of a dezincing machine, any kettle of suitable capacity, and equipment for the handling of one-ton chlorine cylinders. As shown in Fig. 1, the dezincing machine consists of a compact assembly, suitable for handling by overhead crane, of the following units: (1) mill-type motor; (2) reduction gears, air-cooled; (3) variable-speed motor control; (4) pump with capacity 8 to 12 tons per minute; (5) cast-iron reaction cylinder. The dezincing kettles used in several lead refineries range in size from 110 tons lead capacity to 225 tons capacity.

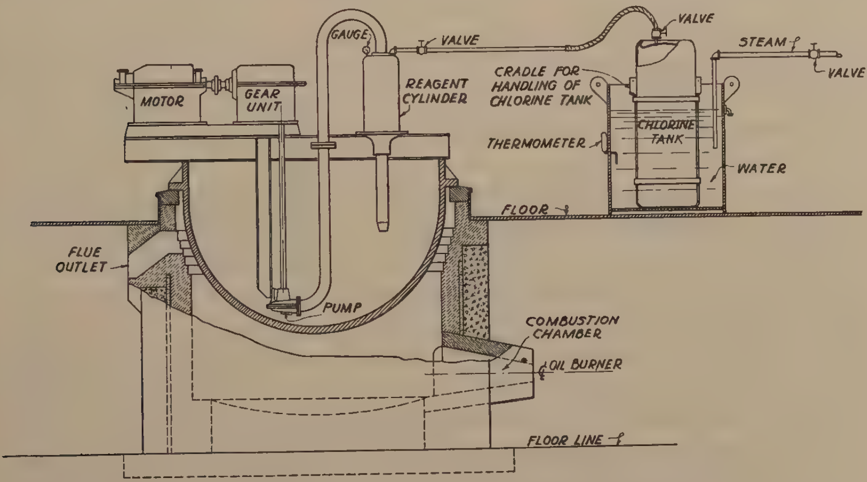


Fig. 1.—Betterton chlorine dezincing machine.

Chlorine Equipment.—We have found it best to purchase chlorine in one-ton drums because these are easily handled without extensive storage facilities for liquid chlorine, which would be required for chlorine received in tank cars; because they are safe, and yet contain a reasonably large amount of chlorine per unit for our purpose. A special drum carrier, as shown in Fig. 1, has been developed for handling and weighing the one-ton drums in and out of the refinery.

When discharging the drums into the reaction cylinders of the dezincing machines, a drum is set vertically in a tank of water provided with an open steam line and thermometer. The water is heated up to 70° F. and not to exceed 90° F. This will allow approximately 400 to 500 lb. chlorine per hour to flow as a gas from the drums. If more is desired, both valves may be connected with separate lines to the reaction cylinder and the quantity increased. Chlorine lines between the drum and the reaction cylinder are made of ½-in. iron pipe, broken by 3 or 4 ft. of flexible steel hose. The hose is fastened to the pipe by special couplings to prevent danger of separation.

Reaction Cylinder.—The purpose of the reaction cylinder is to provide a means of introducing large quantities of chlorine into the lead in a short time. By using an enclosed cylinder, the discharge of which is near the bottom of the kettle, all escape of chlorine into the atmosphere is prevented and complete economy of the use of chlorine obtained.

By properly adjusting the rate of pumping to the rate of chlorine addition, localization of the heat of reaction can be prevented by the rapid passage of lead through the cylinder. This prevents an increase of temperature sufficient to cause any appreciable corrosion of the cast-iron cylinder.

When lead is pumped through the reaction cylinder before any chlorine gas is admitted, the air in the cylinder is gradually carried out with the lead. This is evidenced by the vacuum gradually building to nearly a full vacuum provided the cylinder and fittings entering it are practically airtight.

After the air in the cylinder has been displaced by chlorine gas at the start of the operation, and during the remainder of the time of chlorine addition, conversion of gaseous chlorine into molten zinc chloride is occurring with corresponding reduction of volume. Nearly a full vacuum can be rapidly obtained by cutting off the addition of chlorine at any time during the operation. The explanation of this is that the lead soon exhausts the supply of chlorine in the cylinder and hence a full vacuum results, and the lead raises a corresponding height of nearly three feet in the reaction cylinder.

It will be evident that a vacuum gauge is a good indicator of conditions within the cylinder and is used to maintain them as desired. By allowing chlorine to enter rapidly enough to drop the vacuum to 3 to 5 in. Hg, it is being added as rapidly as the rate of pumping will allow.

The discharge of lead from the reaction cylinder would be in the nature of a vortex were it not for the disturbing effect of the central incoming stream of metal. The result is probably a violent churning action and the discharge pipe is sealed by outflowing metal from the escape of chlorine gas.

By adjusting the vacuum the hydrostatic level of lead is maintained somewhat above the entrance of the discharge pipe in the reaction cylinder, thus confining the chlorine gas within the cylinder and preventing corrosion of the discharge pipe which experience has proven would otherwise occur.

The discharge pipe must be of somewhat larger capacity than the quantity of lead entering the cylinder, otherwise the cylinder would be quickly flooded; however, it is probably advisable not to make it too large. If this is done, no arrest of the lead is effected in the cylinder and as a result it will be necessary to pump more lead relative to any given rate of adding chlorine.

Operation of the Process

As soon as the desilverizing step in the lead refinery has been completed, the desilverized lead is pumped to a dezincing kettle at a temperature preferably 660° F. The dezincing machine is then placed on the kettle and allowed to warm up, the temperature of the lead being maintained at 660° F. The chlorine cylinders in their respective receptacles are then placed adjacent to the dezincing machine and the chlorine outlet valves connected to the reaction cylinder by suitable flexible steel hose, and all joints and connections made absolutely leakproof.

As explained previously, the reaction cylinder operates under a vacuum and any outside air entering the reaction cylinder immediately reacts and produces zinc oxychloride, which is very detrimental in the production of a satisfactory zinc chloride product for the market. The surface of the lead is thoroughly cleaned of all oxide skim because litharge reacting with zinc chloride would produce zinc oxychloride.

As soon as the pump shaft has been found to be free, the motor is started slowly and the speed is gradually increased by the variable speed control until 12 tons of lead per minute are being pumped through the reaction cylinder. This is done in order that the machine may be thoroughly warmed up before the introduction of chlorine gas, and also, if the vacuum gauge registers 28 in. Hg, it proves that the equipment is absolutely leakproof. The speed of the pump is then reduced to about 8 to 10 tons of lead per minute. The chlorine is then admitted slowly and gradually the valve is opened until the vacuum reads 3 to 5 in. of mercury.

During the early stages of chlorining, two gas lines may be connected to the reaction cylinder and chlorine admitted at the rate of 500 lb. per hour. As the action is strongly exothermic, no fuel is required during the dezincing operation; in fact it has been found necessary to admit cooling air to the kettle pit in order that the temperature of reaction may be held within limits and the greatest dezincing speed obtained.

Although zinc chloride does not volatilize under standard conditions until a temperature of 1346° F. is reached, when contained in open kettles a considerable loss and annoyance can occur if the temperature of the bath is allowed to exceed 750° F. From clean surfaces of upflowing lead currents some volatilization occurs which ceases as soon as a thin layer of molten zinc chloride covers the metal.

There is another distinct advantage in not allowing the temperature to become excessive. The zinc chloride skim which collects on the surface of the lead freezes in blocks resembling small ice cakes floating in water and are thereby easily removed by skimming with the ordinary perforated skimming tools. This greatly facilitates the removal of zinc chloride and in well regulated operations the zinc chloride skim is nearly all removed at the same time that the dezincing operation has been completed.

The zinc chloride formed is a deep bluish gray product, and when the zinc has all been practically removed, a white skim, lead chloride, appears, which is easily distinguishable.

The pump should be operated for a short time after the white skim appears in order to obtain zinc finals of 0.005 per cent. The chlorine gas is then shut off and disconnected, the pump allowed to operate for a few minutes in order to thoroughly wash out the cylinder, and then stopped, and the dezincing equipment removed from the kettle.

It has been found that the zinc removal can be calculated by the weight of chlorine used according to the simple reaction between zinc and chlorine. The losses of chlorine are practically negligible, and therefore a 100 per cent value for the chlorine may be used in the above calculations.

The time required for chlorine addition will range from 4 to 5 hr., the over-all cycle time averaging 8 hr. Three charges per kettle unit can be completed in 24 hr. It will thus be evident that the capacity of the process per unit is very large, the maximum capacity of a single kettle unit of 200 tons being 18,000 tons monthly.

Preparation of Marketable Zinc Chloride

The zinc chloride recovered by the dezincing operation will contain variable, minor quantities of lead chloride, lead oxychloride, and roughly about 8 per cent of its weight as lead prills. We have developed commercially two methods of producing marketable zinc chloride as follows:

1. Pure fused zinc chloride by means of a deleading operation which completely removes lead and any traces of other heavy metals.
2. Pure zinc chloride solutions of any desired strengths.

An alternate method, which has been used commercially, particularly in England, is the electrolytic decomposition of zinc chloride. As both the recovered zinc and chlorine would be reused in the same lead refinery, the process is of particular interest in this connection, and a good substitute, should the simpler methods of marketing the product prove unsatisfactory.

Fused Zinc Chloride.—The production of a fused product of the best market quality is accomplished by means of the complete removal of lead and traces of heavy metals by means of a deleading operation with metallic zinc. The chemistry of this latter operation is based on the fact that in the fused salt the lead contained, both as the normal chloride and as the oxychloride, can be completely removed by the simple exchange with zinc in the liquid state forming zinc chloride and zinc oxychloride.

Our procedure is to skim the partly frozen zinc chloride from the dezincing kettle into 3-ton cast-iron lead pots, which must be thoroughly dry and free from iron rust, to prevent any contamination of the product with iron. These pots are immediately discharged into the deleading kettle, which may be of any convenient size. For large operations a kettle of 40 tons lead capacity, and treating approximately 7 tons of zinc chloride is preferable. For small operations, a kettle of 15 tons lead capacity is generally used.

A light fire is maintained on the deleading kettle to prevent the salt from absorbing moisture from the air, and when completely charged, the temperature is raised to 740° F., properly liquefying the salt for good deleading operations.

As an example of this practice, 7 tons of zinc chloride yielded 1120 lb. of lead from the prills, to which was added 175 lb. of metallic zinc; producing a zinc-saturated lead and excess zinc in a mushy crust equivalent to 13.51 per cent zinc. Combined lead was approximately 2.5 per cent, or 350 lb., and required an equivalent of 125 lb. of zinc.

There are two methods adopted for deleading; namely, the molten zinc chloride may be forced down through the metallic bath, or the zinc-lead alloy may be dispersed through the molten salt. Both practices employ a pump for the operation and either method gives satisfactory results.

The time required for this chemical exchange or deleading operation will range from 4 to 10 hr., during which time the temperature is maintained uniformly at 740° F. A thin crust of zinc chloride freezes over the top of the kettle and effectively prevents any loss by volatilization.

When tests show that the lead has been completely removed from the molten zinc chloride, the pumping is stopped and the molten zinc chloride allowed to settle for one hour and then either pumped or tapped into suitable shipping containers. The lead-zinc alloy is returned to the desilverizing process in the lead refinery for utilization of its zinc content.

The product produced is a pure, fused zinc chloride, rather unique in that it is anhydrous. It can regularly be produced free of heavy metals and with a water-soluble zinc chloride content of 99 per cent or somewhat more, the remainder being water-insoluble, or basic zinc chloride. Owing to its method of manufacture, it contains no alkali chlorides, ammonium chloride, sulfates, or carbonates.

Production of Zinc Chloride Solutions.—The methods of purifying and producing zinc chloride solutions of any desired commercial strength and purity are well known and not contemplated in the scope of this paper. It is sufficient to state that the salt produced in the dezincing operation forms an excellent base for the economical production of such marketable solutions. In this case the deleading operation, of course, would be eliminated.

Acknowledgments

The chemistry of the dezincing and deleading processes was well understood before the inception of these processes, so that any advance that has been made in the industry does not lie in this field but in the application of well-known principles and the perfection of such applications. Available supplies of liquid chlorine at constantly decreasing prices has been a large factor.

The greatest initial advance was in the development and perfection of the dezincing machine for rapidly treating large tonnages of lead with chlorine in a most satisfactory manner. The noxious and corrosive characteristics of chlorine are too well known to need comment here, and were largely responsible for a fully justified reluctance on the part of operators to use it.

The present successful commercial application of this process represents in a large measure the painstaking and loyal assistance of many of my associates and I take pleasure in this opportunity to acknowledge this service on the part of the following, who are now or have been members of our company's technical organization: Mr. Robert A. Crites, Mr. Carl Gall, Mr. Henry P. Wagner, Mr. T. D. Jones, Mr. Emil Wurgler, Mr. K. A. Lindner, and Mr. R. F. Cohn.

Electrolytic Lead Refinery, Betts Process, the Consolidated Mining and Smelting Company of Canada Limited

By P. F. McIntyre*

Electrolytic refining of lead was first carried out on a commercial scale at Trail, B. C., in 1903. The capacity at that time was small, and cell-changing operations were managed with chain block and monorail. Development up to 1922, utilizing crane installations and cell additions, attained a production of 100 tons per day. Successive additions from 1922 to 1926 further increased the rated capacity to 396 tons per day. Other improvements in metallurgical practice have gradually increased production, until for the year 1935 it was 448 tons per day. During the first five months of 1936, an average daily production of 504 tons was maintained without increasing the size of the plant.

Lead Refinery

Buildings.—The tank room and the lead-melting and casting equipment are housed in two buildings, which parallel each other and which for the greater part of their lengths are joined by a connecting aisle. All basements, walls, sumps and floors are of concrete. Where exposed to the electrolyte, the concrete has a protective coating of asphalt (220° melting point) over a coat of asphalt paint as a primer. Buildings erected before 1924 are of wood. More recent additions are made of structural steel with gunite siding. A brick building, adjoining the older section of the tank room, houses the slimes-treatment plant. The power house, containing motor generators, air compressors and rectifiers, is constructed of tile.

Cell Construction.—The electrolytic cells are of reinforced concrete lined with asphalt. They are cast in pairs, the outside dimensions of a double cell being 113 in. long by 73 in. wide by 48 in. deep. The bottom is 6 in. thick and the sides, ends and center wall are 4 in. thick. A ledge 3 in. wide and 2½ in. deep is left along the top of the side walls to carry the insulators and bus bars. Reinforcing consists of ½-in. round iron rods. Cell inspection and repair work is done in conjunction with the cell-changing operations. The repair work necessary is usually confined to renewing chipped asphalt, unless a tank has been accidentally broken. Minor concrete repairs can be easily made in place. The broken concrete

---

Manuscript received at the office of the Institute July 3, 1936.

* Superintendent of Refineries, Consolidated Mining & Smelting Company of Canada Ltd., Trail, B. C.

is renewed with a thick mixture of cement and fine sand. The patch is then covered with roofing paper and a layer of asphalt. Cells in the older sections of the plant have been in service for over 20 years.

There are 1116 cells divided into 13 sections. The sections are made up of either 6 or 8 rows of double cells arranged in cascade. The number of cells in a cascade vary from 9 to 4, with the more modern installations favoring the smaller number. The double cells are set 5 in. apart with a drop of 3½ in. between adjacent cells. The rows are set 23 in. apart running lengthwise of the building. Cross aisles run between sections, the widths varying as required by the tank-changing operations.

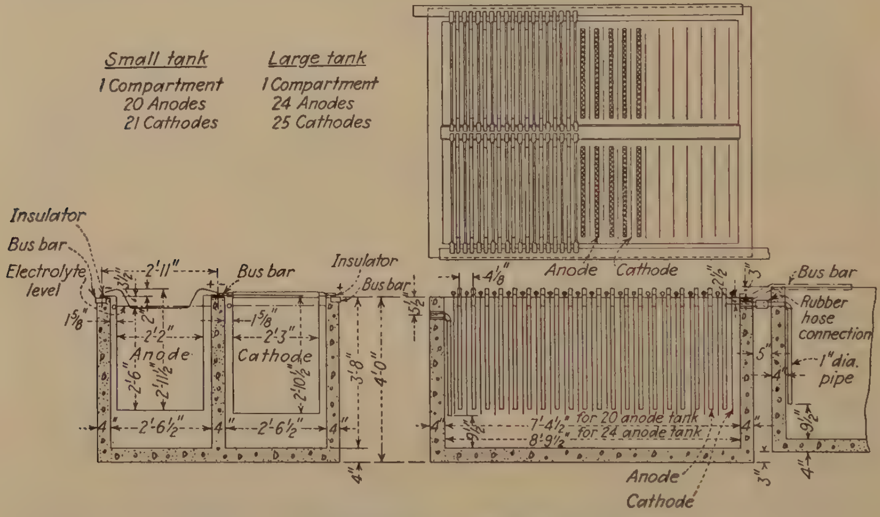


FIG. 1.—ELECTROLYTIC LEAD-REFINING CELL.
Showing arrangement of electrodes; electrolyte circulation piping and bus bars.

The cells are supported on 12 by 16-in. asphalted timbers running crosswise of the building, which in turn are supported by capped 12 by 12-in. pillars set on concrete footings raised above the level of the basement floor. The tank supports also carry a series of aprons and launders of wood lined with roofing paper and asphalt. These aprons and launders convey all solutions siphoned from the cells during tank-cleaning operations to a series of settling tanks. They also serve to catch any leakage or overflow from the cells. The settling tanks in turn prevent entrained slimes from entering the circulating electrolyte.

There is additional storage capacity in the basement equal to about 10 per cent of the total circulating electrolyte. This storage takes care of overflow from the settling tanks, provides for fluctuations in the total volume, and for emergency storage in case of power failure.

Circulation.—Electrolyte is circulated to the top tanks of the cascades by means of 1¼-in. hard-rubber pipes leading from a series of distribution tanks. The electrolyte enters a cell at one side of the top. It is withdrawn at a point 8 in. from the bottom in the diagonally opposite corner from entry, by means of a 1-in. hard-rubber overflow pipe. The overflow pipes are installed by means of hard-rubber nipples and elbows asphalted in place. Nipples between adjacent tanks are connected by pure gum tubing. Electrolyte from the bottom cells of the cascades enters launders, which convey it to the pump tanks from which it is again pumped to the distribution tanks. An air vent is provided in the overflow pipe of the bottom cells in a cascade to prevent siphoning.

Pumps.—Both copper and Monel metal are resistant to corrosion by the electrolyte. Two types of pumps having the parts exposed to the electrolyte made of these metals are in use. For elevating electrolyte to the distribution tanks, plunger pumps are used throughout. A 10-in. copper pipe flanged to a 6-in. pipe forms the plunger and lift sections. A foot valve composed of a perforated plug with disk and spindle is threaded into the bottom of the plunger section. The plunger valve is connected to an overhead eccentric drive by a 2-in. O.D. copper pipe shaft. These pumps, while less economical than the centrifugal type from a power point of view, have given satisfactory service for many years with a minimum of repairs.

Centrifugal pumps of the submerged type are used entirely for all sump and storage service. The shaft is encased in a 6-in. copper pipe, flanged at both ends. The flanges support the impeller casing and the top bearing of the pump. Holes in the 6-in. copper pipe provide spillways for any solution leaking past the lower bearings. The pumps are belt-driven and usually are supported by clamps constructed of timbers, which also act as the motor supports.

Electrolyte.—The electrolyte used in the process is a solution of lead silica fluoride and hydrofluosilicic acid, a representative analysis of which is: sp. gr., 1.210; Pb, 67 grams per liter; free H_2SiF_6, 95 grams per liter; total H_2SiF_6, 142.0 grams per liter.

The circulation of the electrolyte through the cells is at the rate of 3 to 4 gal. per minute. Temperatures vary between 40° and 50° C. Steam coils in the distribution tanks prevent the temperature from going too low and unless the weather is extremely hot, the temperature seldom exceeds the higher figure. Fresh acid is added in proportion to losses sustained, which are at the rate of 2.5 to 3 lb. H_2SiF_6 per short ton of refined lead produced. Sulphuric acid is used when necessary to control the lead content.

J. J. Fingland has fully covered the analytical control work essential to the process[1], and this need not be repeated here. Changes in metallurgical practice since that time will be discussed in a later paragraph.

---

[1] J. J. Fingland: *Trans.* Amer. Electrochem. Soc. (1930) **57**.

Bullion.—A representative analysis of Tadanac lead bullion is as follows: Au, 0.423 oz. per ton; Ag, 49.9 oz. per ton; Cu, 0.035 per cent; Pb, 98.77; Sb, 0.63; As, 0.31; Sn, 0.038; Bi, 0.02.

The bullion is sampled and cast into anodes by the smelting department. The anodes are transported to the refinery in specially designed cars, which permit unloading directly to the electrolytic cells. The weight of the anodes is varied to conform with the required life in the cells and to a lesser degree to the efficiency being obtained. Present practice demands a weight of 8600 to 8800 lb. for a tank of 24 anodes. The submerged dimensions of an anode are 30.125 by 26.25 inches.

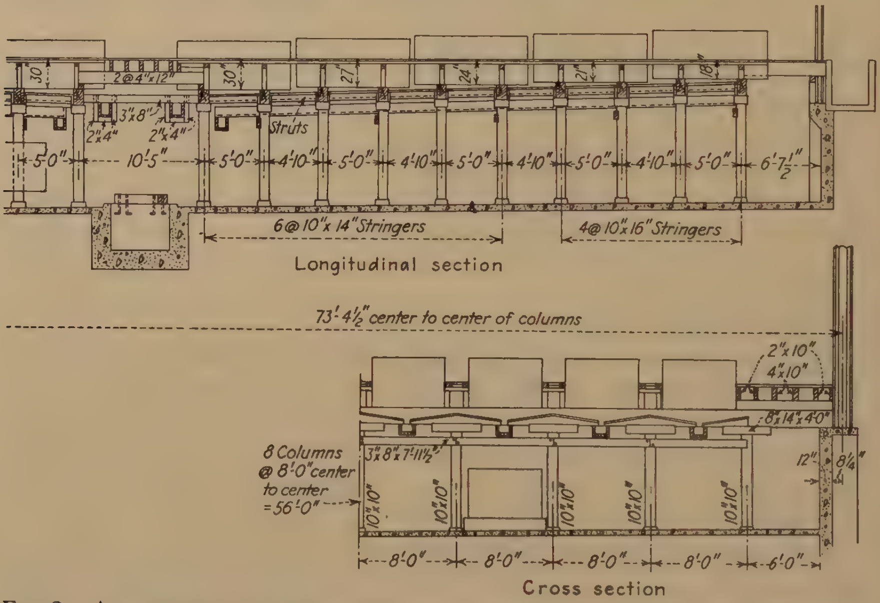


FIG. 2.—ARRANGEMENT OF FIVE-TANK CASCADE, SUPPORTS, RUNWAYS AND LAUNDERS.

Starting Sheets.—Starting sheets are cast from refined lead by ladling the molten metal (temp., 750° C.) into a steel trough, from which it is spilled over a machined, cast-iron plate measuring 39 by 26.75 in. by approximately 1 in. thick. The sheets are trimmed with a knife before removal from the plate. They are stacked on platforms for removal to the sheet-hanging tables. (The submerged area of a sheet is approximately 31.55 by 26.75 in.)

The starting sheets are straightened on a table and then are hung on 1 by ½-in. copper bars. The contact is made by wrapping one end of the sheet 1½ turns around the bar. The bars have a 90° twist 3 in. from each end to provide for maximum contact with the bus bars. They are also offset at both ends to prevent the unwrapping of the sheet. The bars are cleaned by dipping in dilute sulphuric acid, drying and polishing with emery cloth.

The bus-bar current for present operations is 5200 amp. The current density per square foot is 18.5 amp. The initial voltage across a newly set cell is 0.35 to 0.40 volts. This voltage drop increases gradually until it reaches 0.65 to 0.70 volts on the final day of electrolysis.

Cell-changing Operations.—Present operations are on the basis of a six-day anode, a three-day cathode and six-day slimes. After electrolysis for three days, the cathodes are removed from the cells, washed to remove entrained acid and slime, and delivered to the melting pots. Bus-bar contacts having been sponged with electrolyte and polished with emery cloth, new settings of starting sheets are installed. After a second three-day period of electrolysis, the cathodes are removed, washed and sent to the melting pots. The residual anodes are taken to scrap-washing machines, where the slime is removed, and then transported to the scrap-melting pots. The bus bars having been thoroughly cleaned with electrolyte and emery cloth, new anodes and starting sheets are charged. When special grades of lead are required the slime is removed from the anodes at the end of three days electrolysis. Every 24 days the cells are completely emptied for slimes removal and inspection. The electrolyte, to within 6 in. of the bottom, is siphoned to the aprons beneath the cells. The remainder of the electrolyte, plus slime that has fallen from the anodes, is removed by buckets to special cars and hauled to the filters. After cleaning, the cells are inspected for flaws in the asphalt.

All cell-changing operations are carried out by contract labor.

Tank Testing.—Contract labor being employed in the cell-changing operations for the purpose of reducing the cut-out time to a minimum, only nominal care is required from the operators. Six special tank testers or electrode setters are employed to immediately follow up the contractors and provide for the proper spacing of the anodes and cathodes. In addition, groups of six men per shift carry out routine inspection of all cells.

Melting and Casting.—Melting and casting of the refined lead are done in the building that contains the electrolytic cells, so that direct crane delivery of the cathodes to the melting pots is possible. Before August, 1935, 60-ton cast-steel kettles, hand-fired, were used entirely. Since that time a 235-ton welded-plate kettle, fired with pulverized coal, has been in service. Additional similar installations will ultimately replace the smaller units.

After melting, the cathode lead is heated to 950° F. and blown with air to remove small percentages of tin, arsenic and antimony. Depending on the purity of the cathodes, 20 to 60 min. is required for this operation, the end point of which is determined by the characteristic blue colors of the lead fountain. The melting and refining drosses are then circulated through the hot metal to liquate entrained metallics, by means of a centrifugal mixer. The drosses, amounting to 2.5 per cent of the charge, are removed by a perforated skimmer. The metal is then allowed to cool to about 780° F. for casting.

The refined lead is cast by pumping directly to molds set on a motor-driven wheel 20 ft. in diameter. This has a center shaft and under-braced frame. The slip bearing is below the floor and the top bearing and drive are carried on a frame about 3 ft. above the floor. This arrangement does not interfere with crane service and also makes a more stable wheel. The molds are cantilevered from the center shaft. Cooling is accomplished by sprays on the bottoms of the molds. A water seal protects the workmen from steam. A mechanical pig lifter and loader is not used. The lead pigs are loaded by hand to specially designed dump cars, which are operated on 18-in. gauge tracks that pass over two sets of scales to the loading platforms. A spare wheel of similar construction is available for service.

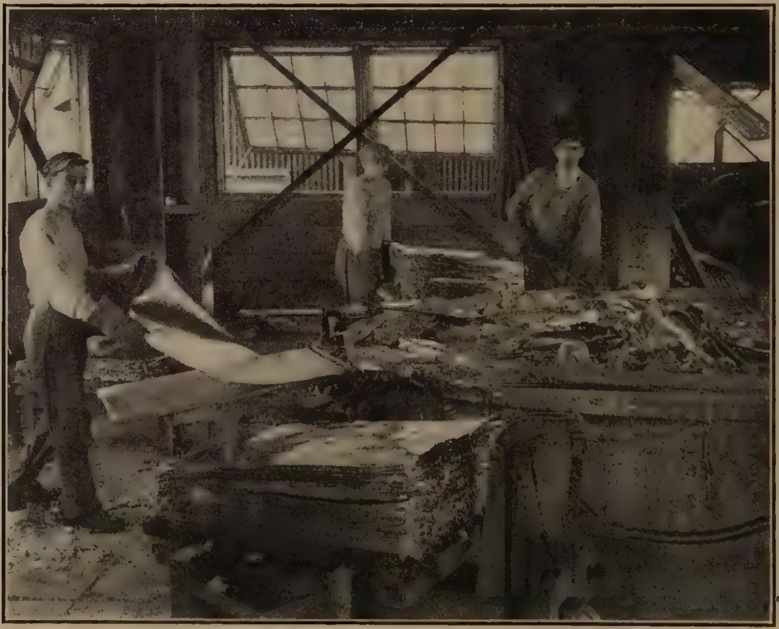


FIG. 3.—CASTING STARTING SHEETS.

Washing Anode Scrap.—The residual anodes with the adhering slime sponge are delivered to racks situated under ½-ton monorail cranes serving the scrap-washing machines. These washing machines consist of motor-driven circular fiber brushes, mounted on shafts that are in turn carried by Monel side frames equipped with brass bearings and Monel tie rods. The power for the brushes is applied through sprocket-chain drives. Brush adjustment is obtained by means of eccentric bearings.

The brush units are mounted on concrete, asphalt-lined, collector tanks, the center line of the brushes being on the same level as the tank overflows.

The slime sponge is removed by lowering the anode scrap between the brushes and withdrawing against the brush rotation, the collector tank having been previously filled with electrolyte or filter solution. Overflow from this tank goes to a slimes pump tank. The cleaned scrap anodes are stacked for removal to scrap-anode melting pots.

The scrap-anode bullion is melted in 60-ton kettles adjacent to the refined-lead melting plant. It is then recast into anodes on a wheel of design similar to that of the lead-casting wheel. This wheel has 16 molds with stationary pans, to which are hinged the head pieces or lug-forming portions of the mold. The anodes are removed from the wheel by a ¼-ton monorail crane and set in racks ready for recharging to the cells.

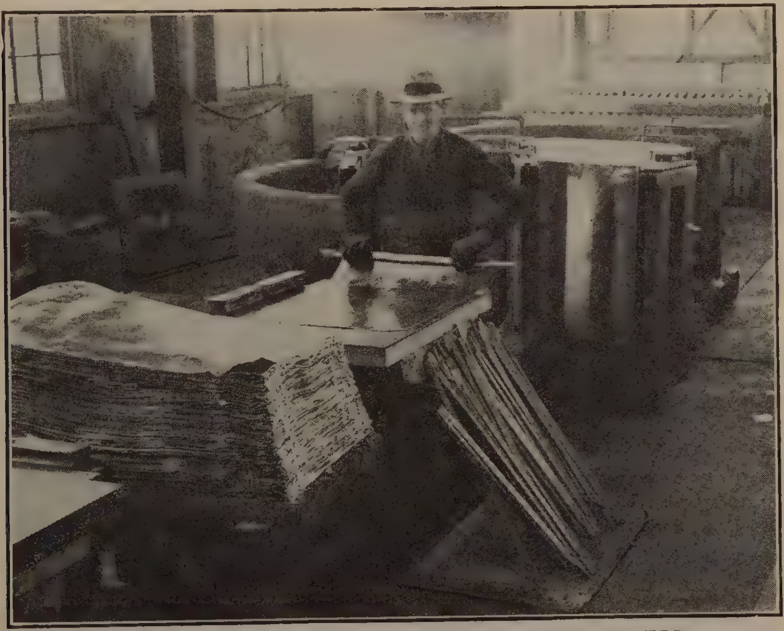


Fig. 4.—Preparation of starting sheets for cells.

Slimes Washing.—The filtration of the slimes sponge is accomplished in cylindrical concrete tanks with standard asphalt linings. A false bottom covered with cocoa matting and 4-oz. duck supplies the filtering medium. Vacuum is applied to the bottom of this filter through a copper connection bolted and asphalted in place. Duplicate vacuum receivers are interconnected, permitting the withdrawal of filter solution without interrupting the filtration process. A 6-in. Nash Hytor pump supplies the vacuum.

In the washing process the mother liquor is first drawn off until the residual cake shows signs of cracking. Successive water washes are then added until the effluent solutions are reduced to 0° Bé. The cake is then allowed to crack, and is successively tamped and cracked until the entrained water is reduced to a minimum. The usual moisture content varies between 66 and 70 per cent. The washed slime is loaded into special cars and transported to the silver refinery by crane.

At present a 48-in. perforated basket-type centrifuge is under test for washing slime. To date this machine has handled more than 2½ tons of slime (dry weight) in 24 hr., with a final moisture content of 45 per cent. The wash water required is only 25 per cent of that required by the vacuum filters. A centrifugal plant to handle the total slimes production is under consideration.

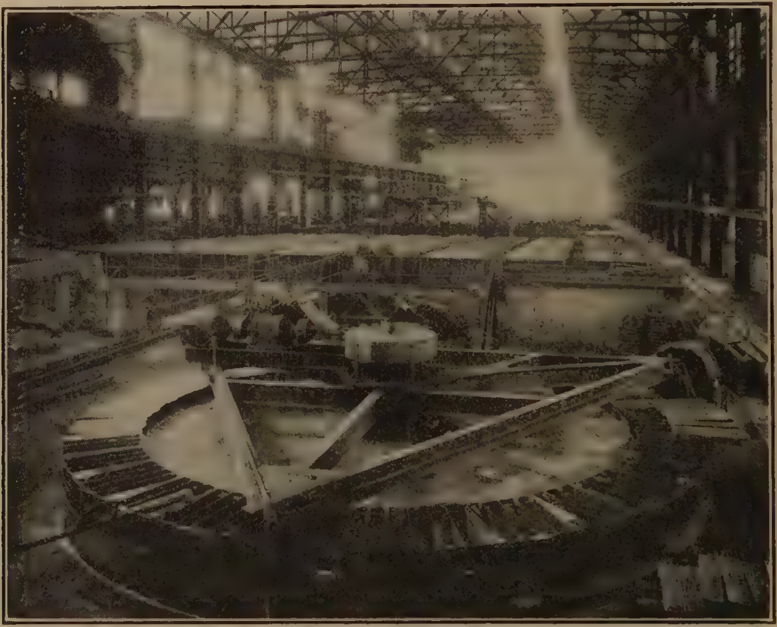


Fig. 5.—Cell room with lead-casting wheel in foreground.

Basis of Operation at Trail

The operation of an electrolytic lead refinery on a six-day anode, three-day cathode basis, with the attending high labor cost over an eight or ten-day anode cycle, may appear out of line to readers familiar with the process. A consideration of the problem as it affects this plant will explain the reasons for its choice.

In the electrolytic refining of lead bullion, it is imperative to have present in the bullion impurities that will produce a slime sponge having physical properties that will permit its adherence to the residual anode. Failing this condition, the slime will slide from the anode face and become entrained in the cathode deposit. Antimony is the chief impurity required to obtain the necessary condition, the amount required depending in part on the current density used. In former operations, when a deficiency of antimony occurred, it was customary to return reject products high in antimony from the silver-recovery plant to the lead blast furnaces. Present practice, utilizing more anode-casting and cell-changing labor and a shorter anode life, has made possible the production of market lead without any control of the antimony content.

Operations prior to 1934, utilizing an eight-day anode and four-day cathode and allowing the slimes to remain on the anode during the full period of electrolysis, had proved that 0.75 per cent antimony was required for good working conditions. Current densities used ranged between 16 and 17 amp. per sq. foot.

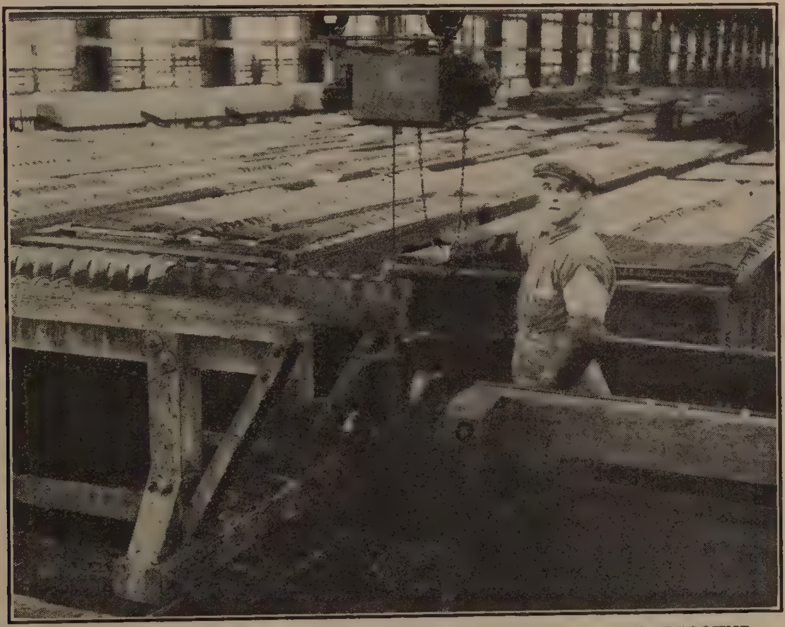


FIG. 6.—CELL ROOM WITH SCRAP-WASHING MACHINE IN FOREGROUND.

Late in 1933 the practice of washing the slime from the anodes at the end of the fourth day was inaugurated. Immediate improvement in the grade of the cathode deposit was noted. As similar results had been obtained for some years when operating part of the plant on a six-day anode basis for the production of special grades of lead, it was decided to investigate the possibilities of a six-day anode at increased current densities. The results have been most satisfactory. An improved grade of cathode has been obtained with current densities up to 18.5 amp. per sq. ft., which is the limit of the present available power supply. An improvement in the current efficiency of 5 to 7 per cent has also resulted. Tests run in experimental cells of plant size have shown that the upper limits for current densities in electrolytic lead refining have by no means been reached.

Mention has been made of the fact that the voltage drop across a cell increases from 0.35 volts to 0.7 volts during the period of electrolysis. The current density, composition and temperature of the electrolyte and the condition of the contacts are the controlling factors of the initial voltage, of course. These factors, however, do not vary to any appreciable extent from the start to the finish of the period of electrolysis. It is to the face of the anode we must look for the change in conditions resulting in this gradually increasing resistance. Here, as electrolysis proceeds, we are steadily substituting a layer of slime comprising in part the impurities originally contained in the bullion. This slimes layer, by weight, is only 1.5 to 1.75 per cent of the bullion in which it was originally contained but has practically the same volume. We can see, therefore, that the slimes layer is, in fact, a metallic sponge through the interstitial spaces of which the electrolytically dissolved lead must pass to the electrolyte and thence to the cathode. It has been proved that the free acid content of the solution within these interstices becomes less as the slimes layer increases. Conversely, the lead fluosilicate content increases. We have thus obtained a layer relatively high in resistance to the passage of the current. When electrolysis is allowed to continue for a sufficient length of time, the voltage drop across the cell will reach a point at which the outer face of the slimes layer will commence to dissolve. Under these conditions antimony, arsenic, tin if present, and bismuth to a lesser degree, will be dissolved and plated on the cathode. Under these conditions also the outer layer of slime will disintegrate, thus permitting silver and additional quantities of the metals mentioned to be mechanically transferred to the cathode.

The accumulative resistance of the slimes layer has been discussed at length. Other resistances incidental to lead electrolysis, with the exception of electrolyte resistance, are parallel to those found in the electrolytic refining of copper, and need not be discussed at length here. A representative analysis of the electrolyte with regard to the free and combined acid has been given. Considerable latitude in these constituents is permissible. It is also true that metallic impurities common to the process are not seriously accumulative. The decomposition products of gelatinous addition agents, however, have accumulative effects, which, if not controlled, may have considerable adverse effect on the conductivity of the electrolyte.

At Tadanac a high grade of glue has been used for years as an addition agent. Additions have been made at the approximate rate of 1½ lb. of glue per short ton of lead produced. A considerable portion of this glue is ultimately decomposed to amino acetic acids, which have no outlet from the system. High mechanical acid losses incidental to pioneer operations at Tadanac provided this outlet. Later, dilution of the electrolyte accompanying plant expansion offset any accumulation. More recently it has been necessary to withdraw a portion of the electrolyte from the system. The electrolyte withdrawn is treated with sulphuric acid to remove the lead and then shipped to an acid-recovery plant. About 75 per cent of the contained acid is recovered. More recently Goulac has been substituted, in part, for glue as an addition agent. The absence of nitrogen from this product may eliminate or at least reduce the necessity for electrolyte purification in future operations.

SILVER REFINERY

The silver-refinery process may be briefly described as a furnace operation in which the slime is first melted to a metal, from which the base metals contained are successively eliminated by oxidation. The resulting doré metal is parted by the sulphuric acid process. The parted gold is melted and shipped to the mint without further refining. A bluestone plant recovers the copper used in the process and a bismuth-recovery plant is operated intermittently for the elimination of bismuth.

The furnace department consists of eight furnaces of conventional design. About 10 to 12 per cent slag is formed in the melting operation. This slag receives a reducing treatment for the recovery of the contained precious metals and is then shipped to the lead blast-furnace department. The metal recovered from the slag is treated with the metal from the primary slimes melt.

While some arsenic and antimony are oxidized and pass off as fume in the melting operation, the bulk of these metals is fumed off in a "burning down" step. Pulverized coal is used as fuel in the melting and burning down furnaces. A Cottrell plant is the dust-collecting medium. The flue dusts do not receive any further treatment and are placed on a stock dump.

The residual metal from the burning down step is further refined in a coke-fired furnace. This metal still contains about 12 per cent antimony. A lead antimonite slag is first removed. As refining proceeds the litharges formed contain increasing amounts of copper and bismuth. When necessary, niter is used for the final refining of a doré charge. The slags from the doré furnaces are wholly or in part re-treated for the recovery of bismuth. A lead-bismuth metal carrying 20 to 25 per cent bismuth is recovered and the residual slag is returned to the smelter.

Bismuth Recovery.—The lead-bismuth metal is first drossed for the separation of copper. The contained precious metals are removed by the Parkes process. Pattinsonization of the desilverized metal results in a lead-bismuth metal relatively free from impurities. This metal in turn is electrolytically refined by the Betts process. The resulting slime is melted and refined to market bismuth of a high degree of purity.

REPAIR WORK

The refinery department maintains a repair shop and crew for routine plant repairs. Repairs of major proportions are made by the main mechanical departments, which service all divisions of the Tadanac operations.

The Betts Process at Oroya, Peru, S. A.

By T. E. Harper, Jr.,* Member A.I.M.E., and Gustave Reinberg†

Electrolytic refining of all lead bullion produced at the Oroya smelter of the Cerro de Pasco Copper Corporation has been adopted as standard practice. A pilot refinery with a capacity of 25 metric tons daily has been in operation since June, 1934, and a new refining unit having an initial capacity of 100 tons per day is under construction. This program has been made possible by certain modifications of the usual Betts refining process[1], developed at Oroya, which have the effect of making the purity of the lead produced, and the acid loss incurred in operating the process, entirely independent of the amount of impurities in the original bullion. The modified process, as developed and at present used, treats impure bullion direct, without presoftening or other prerefining step, except that if the bullion carries tin it is desirable to detin before casting into anodes, since tin carries over to some extent to the cathodes.

The refining process developed differs from usual Betts practice in two essential particulars: the anodes are cast thinner and replaced at more frequent intervals, and anode slimes are washed by a system of counter-current dipping, prior to their removal from the surface of the anode scrap. Limiting the period of anode corrosion insures a cathode of high purity, since solution of impurities at the anode can occur only if the thickness of the anode slime blanket, and hence the voltage drop across it, becomes greater than a certain critical value. The dip washing system operates to prevent acid losses, by recovering the highly concentrated, nearly neutral lead fluosilicate solution present in the pores of the slime blanket on the corroded anode, and doing this in such a way that there is no opportunity for chemical decomposition to occur. The best illustration of the efficacy of these two expedients may be secured from records of more than a year's operation of the 25-ton pilot plant, during which period the acid losses were less than 2 lb. of 100 per cent hydrofluosilic acid (H_2SiF_6) per ton of lead produced, and typical assays of bullion and refined lead were as shown in Table 1.

Manuscript received at the office of the Institute Sept. 8, 1936.

* Director of Research, Cerro de Pasco Copper Corporation, Oroya, Peru.

† Research Engineer, Cerro de Pasco Copper Corporation.

[1] See U. S. Patent No. 1913985; Mexican Patent No. 33532, issued Oct. 7, 1932; Canadian Patent No. 341290, issued May 1, 1934.

TABLE 1.—*Typical Assays during Operation of Pilot Plant*

	Assays, Per Cent					
	Pb	Cu	As	Sb	Bi	Ag
Bullion treated..........	90.1	0.12	1.9	3.3	4.4	0.14 (40.7 oz. per ton)
Lead produced..........	99.998	0.0001	0.00005	0.0004	0.0005	0.000008 (0.002 oz. per ton)
Slimes..................	19–20	0.8	12–13	23–24	30–31	280 oz. per ton

In extensive test work, anodes containing 80 per cent lead or less have been refined by shortening the anode-corrosion period appropriately, with no increase in cathode impurities or acid losses over those given above.

ANODE CORROSION

Inasmuch as the amount of corrosion is the vital feature in the question of cathode purity, it will be interesting to examine the mechanism of its effects in some detail. It is a fundamental characteristic of electrolytic lead refining that practically all of the impurities commonly associated with lead bullions are more "noble" than lead, and therefore remain undissolved at the anode during electrolysis. If present in sufficient quantity, such impurities remain attached to the anode in the form of an adherent slime layer or blanket, which retains the original physical shape of the anode. In fact, the first requisite for the production of a pure cathode is to have enough impurity in the anode to furnish a thoroughly adherent slime, from which no particles will float off in the electrolyte and thus become entangled with the cathode deposit. Incidentally, the presence of adequate impurities to prevent the danger of mechanical transfer of slimes to the cathode will also permit application of the countercurrent dip washing to be described later.

As corrosion of an anode proceeds, the electrolytic current must be carried by the solution in the pores of the slime blanket remaining on the face of the anode. This gives rise to an ohmic voltage drop across the blanket, which increases as the thickness of the blanket increases, and, for any given thickness, increases with increasing impurity concentration, because of decreased porosity. If this voltage drop attains a value equal to or greater than the difference between the solution potentials of an impurity present in the blanket and that of lead, such impurity will be dissolved and transferred electrolytically to the cathode. The voltage drop across the anode slime blanket naturally produces a corresponding rise in the total voltage across the cell during the life of the anode, and if this voltage rise is kept below its critical value, which for practical purposes may be taken at 0.2 to 0.3 volt, equivalent to an over-all cell voltage of 0.50 to 0.60 volt under our conditions, and if the slime blanket is sufficiently adherent, pure cathodes will be obtained irrespective of the composition of the anode.

There are two ways in which the voltage drop across the anode slime layer may be limited; adjustment of the current density, and adjustment of the total thickness attained by the slime layer—i.e., the life of the anode. In our work, a current density of 14 to 15 amp. per square foot of anode surface was adopted, and at this density the following approximate limits of anode-corrosion period were established: (1) for bullions containing over 90 per cent lead, four-day anodes; (2) for bullions containing between 80 and 90 per cent lead, two-day anodes; (3) for bullions containing less than 80 per cent lead, one-day anodes or less; all anodes are scrapped at the end of the corrosion period. The third period, of course, is one that would scarcely occur in practice, but was investigated to some extent experimentally, to demonstrate that pure cathodes could be obtained from anodes containing as little as 50 per cent lead.

Thanks to the ease with which lead bullion may be melted and cast, these reductions in anode life do not lead to exorbitant increases in operating costs, although anode scrap amounts to about 40 per cent with four-day anodes. With a plant properly designed to meet the conditions, the use of four-day anodes should show only a slight difference from conventional eight-day practice, and extends the applicability of the process from bullions with 97 per cent lead or more to bullions containing 90 per cent lead or more, in addition to producing a higher grade of refined lead. For the special types of bullion that require it, the use of two-day anodes would not under normal conditions be unduly expensive, as compared with alternative methods of treating such material. Of course, in the last analysis, the question of applicability is entirely dependent upon local conditions; we merely wish to emphasize that the solution found for the technical problem is not incompatible with economic requirements.

Acid Loss and Dip Washing

With the production of cathodes of high purity, the metallurgical requirements of the process as applied to low-grade bullion had been met. The attainment of a low acid loss, however, particularly at Oroya, is a vital economic requirement of the Betts process, and it was here that attempts to treat low-grade bullion had encountered the greatest difficulty in the past. A roughly quantitative relationship between acid losses and grade of bullion treated was, in fact, assumed. The justification for this assumption is a little doubtful. It was, nevertheless, true that it had been found difficult to keep acid losses within reasonable limits at best, and impossible with low-grade anodes.

A potential source of relatively enormous acid loss is inherent in the process, since the pores of the anode slime blanket become filled with a highly concentrated solution of neutral lead fluosilicate as corrosion proceeds. Limiting the life of the anodes to four days or less helps this situation by reducing the maximum thickness of the blanket and the final concentration reached in the pores; also, the absence of electrolytic solution of impurities by overcorrosion avoids the possibility of loss through the formation of insoluble compounds such as antimony fluosilicate. The problem then resolved itself into recovery of the solutions remaining in the slime pores at the conclusion of electrolysis.

If the slimes are removed from the anode scrap before they are washed, as is the usual practice, it is very difficult to avoid mechanical losses, and there is some evidence that insoluble fluosilicate compounds may be formed spontaneously in the slimes under certain conditions. Also, when the slimes are washed in tanks and filter-pressed, dilute wash liquors are usually produced, which must be evaporated, and this operation may give rise to decomposition losses, in addition to being a nuisance. Since the slimes produced from low-grade bullion are naturally very adherent, an ideal solution of all these difficulties was found in a system of countercurrent dip washing. This consists merely of passing the corroded anodes, immediately after removal from the cells and with their slime blankets still attached, through a series of dip tanks in which they meet a small flow of wash water traveling in the opposite direction. This removes the strong liquor in the pores by diffusion, and since the flow of wash water is adjusted to balance the volume removed from the circuit in the pores plus normal evaporation from the cells, there are no weak wash liquors to be concentrated. A series of four dip tanks serves to reduce the soluble fluosilicate in the pores to about one pound per ton of lead produced. All other losses, including insoluble fluosilicate compounds in the slimes, loss on cathodes, etc., amount to less than one pound, so that the pilot plant has operated for a prolonged period with an over-all loss of under 2 lb. per ton of refined lead. Loss by actual decomposition in the cells is evidently negligibly small, if it occurs at all under these conditions.

Development

In all respects other than the foregoing, the refinery is operated substantially identically with standard Betts plant practice. Provision has been made, of course, for casting accurately the thin anodes required, and for handling them expeditiously, and a few other mechanical refinements have been developed. The standard lead fluosilicate-hydrofluosilicic acid electrolyte is employed, and has been found to operate satisfactorily over a wide range of concentrations. The total hydrofluosilicic acid concentration is normally kept between 100 and 150 grams per liter, with lead between 60 and 100 grams per liter, equivalent to 60 to 80 grams of free acid per liter. The lead concentration in the electrolyte tends to build up slowly during operation, the excess being removed periodically in a stripping cell equipped with insoluble (graphite) anodes.

The initial laboratory experiments were made in small glass battery jars, containing a single anode 6 in. square. Semiplant-scale work was then conducted for an extended period, at first with 400-amp. cells, and later with two commercial-size tanks using 4000 amp. The results obtained throughout this work were entirely confirmatory of the original deductions; in fact, the purity of the lead produced has tended to increase, and acid losses have tended to decrease, with the increasing scale of operations.

Present Pilot Plant

The present pilot plant is a complete commercial unit with a daily capacity of 25 tons of refined lead. The kettle house is of steel construction and houses four 70-ton oil-fired kettles, two of which are employed for melting bullion and two for the melting of cathodes. Anodes and refined bars are cast on mechanical casting wheels of similar construction, the bullion wheel having 12 molds for 26 by 36-in. anodes, and the refined-lead wheel 12 five-gang molds for 100-lb. bars. Electrodes are transported between the kettle house and the tank house in narrow-gauge cars operated by storage-battery locomotives.

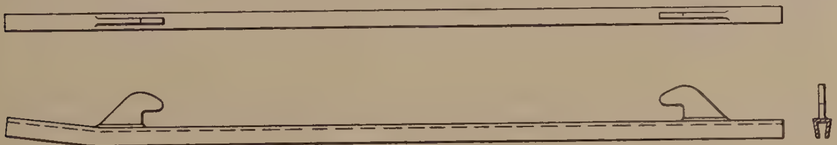


Fig. 1.—Copperplated steel cathode bar.

The tank house is a brick building containing 64 electrolytic cells and 16 anode wash tanks. There are 24 anodes and 25 cathodes in each cell, the normal circuit current being 4700 amp. Power is received from the smelter substation at 2200 volts, three-phase, 60 cycles a.c. and is converted to direct current by a synchronous motor-generator set with a rated output of 5000 amp. at 30 volts. The cells and wash tanks, constructed of concrete and lined with Trinidad asphalt, are 8 ft. 10 in. long, 2 ft. 7 in. wide, and 3 ft. 10 in. deep inside. Electrolyte is circulated through a hard-rubber piping system by means of rubber-lined centrifugal pumps. The average temperature of the electrolyte is 37° C. and the flow is about 3 gal. per minute per cell. The tanks are arranged according to the Walker system, and are serviced by electric monorail hoists of 3 tons capacity. Only one cell at a time is short-circuited for the purpose of changing electrodes, and as this operation requires but a few minutes, practically full production is maintained at all times. Experience has shown that the accumulation of detached slimes in the cells is so slight that the tanks would not require draining for cleaning purposes over a period of at least five years. A departure from standard practice occurs in connection with the cathodes. The starting sheets, 27 by 37 in. immersed, are cast upon an inclined table in the usual way, but the supporting rods are made of copperplated steel, and are formed with a dovetail slot into which the sheet is integrally cast (Fig. 1). Shallow rounded grooves in the starting-sheet table form ridges in the starting sheets, which give additional stiffness to the sheets. The finished cathodes are dropped into the melting kettle from a crane, and the cross rods subsequently are skimmed from the surface of the melted lead. This procedure eliminates the labor incident to wrapping or otherwise attaching the starting sheet to the bar, makes a somewhat stiffer sheet, and affords a better electrical contact with the cross bar than is usually obtained.

The pilot plant is being kept in operation pending completion of the new 100-ton refinery, which is expected to begin operation early in 1937. No difficulties of serious moment have been encountered in operating the pilot plant, in spite of the fact that only native labor, totally inexperienced in this class of work, was available when work in the plant was started.

Electrolytic Solder

By R. P. E. Hermsdorf* and Max Heberlein,† Members A.I.M.E.

(New York Meeting, February, 1936)

The electrolytic refining of metals for the removal of undesirable impurities has become a recognized necessity in the nonferrous field. Copper, lead, zinc, nickel, silver and gold have been produced in this manner for years. The United States Metals Refining Co., realizing that considerable quantities of lead and tin could be made available to the trade if a satisfactory method of purification of these metals could be established, decided to investigate the possibilities of electrolytic solder.

In cooperation with Dr. Edward F. Kern, of the School of Mines at Columbia University, the company developed a process of electrolytic refining of lead-tin alloys using a tin-lead fluosilicate electrolyte. A pilot plant was installed in November 1927, and the commercial unit was put in October 1929. Since that time thousands of tons of electrolytic solder have been produced in this plant and consumed by all branches of industry that use solder.

Older Methods of Producing Solder

In the early days practically all solder was made by melting together virgin lead and tin in the proper proportions to meet specifications; then the solder was cast into the commercial shapes required. Today the base of most solders comes from scrap or secondary materials. Ordinarily solder is produced from secondary materials either by sweating solder-bearing scrap or by smelting lead and tin-bearing drosses, residues and similar materials. When solder is produced from scrap by sweating, clear solder is collected directly. It is then given some kind of kettle refining and usually blended to specification with virgin metals before it is cast into finished shapes. In producing solder from drosses and residues, the materials are usually first given a reducing smelting treatment from which a crude solder is obtained. This crude solder may be refined in several ways, but usually the first step is a furnace liquation to remove the bulk of the copper, which is followed by one of the more or less complicated methods for the removal of antimony and other impurities.

Manuscript received at the office of the Institute Dec. 2, 1935.

* Production Superintendent, U. S. Metals Refining Co., Carteret, N. J.

† Director of Research, U. S. Metals Refining Co.

These refining methods usually remove only the base metals, such as copper, zinc, arsenic and antimony, and have no effect on gold and silver, but since the precious metals are found in a large portion of the tin-lead material available, it is necessary to consider their presence in refining solders from these sources. In the old method of refining, the separation of precious metals from solder was not economically feasible, whereas in electrolytic refining the separation is readily accomplished.

ELECTROLYTIC PROCESS

Advantages.—In comparison with the usual furnace and kettle methods of refining, the electrolytic process stands out as a marked improvement in the art of producing high-grade solder. The outstanding advantage of the electrolytic process is the possibility of removing in one operation both the base impurities and precious metals to an extent almost impossible to reach by ordinary methods.

Impure Solder.—Starting with the crude tin and lead-bearing materials, the first step in the operation is the production by smelting of an impure solder containing impurities varying in amount according to the materials treated. A blast furnace, reverberatory or electric furnace may be used for this purpose.

A thorough investigation revealed the fact that the majority of impurities in the crude alloy are present in the form of intermetallic compounds such as Cu_2Sn, Cu_3Sb, Cu_3As, $SnSb$, $SnAs$, Fe_3Sn, $FeSn_2$, $FeSb_2$, Fe_3Sb_2, Fe_3As_2, and many others. The presence of the intermetallic compounds explains the peculiar behavior of some impurities during the electrolytic refining process. Such impurities, which, according to their relative position in the electromotive series, would be expected to deposit with the lead and tin on the cathode, or go into solution, actually enter the anode residue with the less electropositive metals.

Preliminary Treatment.—The preliminary treatment of the impure solder before electrolysis consists of a liquation to remove most of the copper followed by the well-known method of decopperization by stirring sulphur into the cool liquid metal. The copper content is thus, ordinarily, reduced to below 0.5 per cent. If impurities such as antimony and arsenic are present in amounts too high for smooth electrolytic operation, other treatments may be resorted to for their partial removal before casting into anodes. Metals standing higher than lead and tin in the electromotive series do not occur ordinarily in appreciable quantities.

The preliminary treatment is determined by the amount and nature of the impurities present. Its object is to reduce the total content of undesirable impurities to as low an amount as is practically economical before electrolysis, and at the same time to produce a residual anode slime that will adhere to the anode without producing passive anodes, and one that will not because of its dense, tough characteristics, become difficult to remove from the anode scrap. Slimes that do not adhere to the anode either drop to the bottom of the tank or float in the electrolyte, depending somewhat upon their composition and relative amount. A floating slime is to be avoided because an impure deposit of solder will result.

Permissible Analyses.—Regarding the total amount of impurities permissible for economic electrolytic treatment, anodes with the following typical analysis have been electrolyzed without difficulty: 76.9 per cent Pb, 13.72 Sn, 7.75 Sb, 1.1 Cu, 0.1 As, nil Fe. The cathode deposit obtained in this run formed bright, smooth and dense. The residual slimes produced from the anodes contained, in addition to the impurities, a considerable amount of tin in the form of stannides of these impurities, and also a small amount of lead. This demonstrated clearly the metalloidic character of tin, and the strictly metallic chemical behavior of lead, which obviously does not form intermetallic compounds with the other metals present. An attempt to electrolyze anodes containing 65.7 per cent Pb, 14.36 Sn, 9.5 Sb, 8.57 Cu, 0.48 As, 0.73 Fe resulted in failure, inasmuch as the anodes became passive, and were completely insoluble after several hours. Obviously, almost the total tin present formed intermetallic compounds with the impurities, thus rendering the anodes inert. The metal was actually not an alloy but rather a fused mass of chemical compounds with metallic lead as a binder. These two test runs indicate clearly that the electrolytic operations become less practical with increasing amounts of impurities in the anode metal. The economical limit was found to be approximately 10 per cent total impurities.

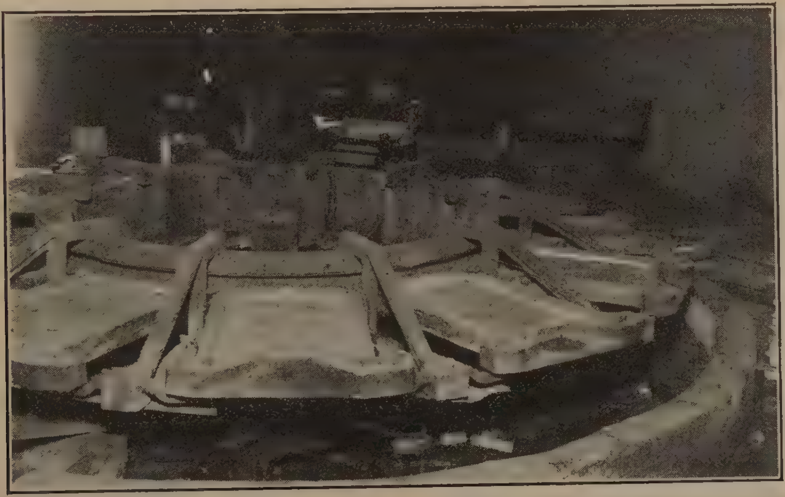


FIG. 1.—ANODE CASTING WHEEL, SHOWING POURING LADLE, PUMP AND KETTLE IN BACKGROUND.

Anodes.—After the preliminary treatment, the metal is ready to be cast into anodes, which is done by pumping the metal from a 30-ton kettle into a wide-spouted casting ladle. This ladle is mounted as one self-contained unit with a small casting wheel carrying 12 anode molds (Fig. 1). In principle, this complete installation resembles the anode-casting arrangement of a copper refinery. It is possible to cast 30 anodes per hour, a casting capacity of 5 to 6 tons per hour. The cast anodes are 36 in. long, 24 in. wide and 1¼ in. thick and weigh between 350 and 400 lb., depending somewhat on the ratio of tin and lead content.

During the years that the plant has been operating, anodes within the ranges shown in Table 1 have been commercially electrolyzed. However, by blending several lots of crude solder, the analysis is usually kept at about the composition given in the last column of Table 1.

Table 1.—*Composition of Anodes*

	Occasional Analysis		Usual Analysis
	Low	High	
Pb, per cent	49.64	83.42	62
Sn, per cent	13.86	47.84	35
Sb, per cent	0.18	8.05	2
As, per cent	Tr	3.25	0.25
Cu, per cent	Tr	3.75	0.05
Au, oz. per ton	Tr	0.20	0.05
Ag, oz. per ton	2.3	145.2	30

Cathodes.—At present, cathode starting sheets are made by the apparatus devised by J. F. Miller, Trail, B. C., by pouring molten, electrolytically refined solder from a trough over an inclined polished steel plate having the exact dimensions and shape desired (Fig. 2). The two extended hangers on the cast sheet are turned back over a copper rod and spot-welded to the main sheet by means of hot soldering irons. The cathode sheet is 38 in. long and 26 in. wide.

Electrolyte.—The electrolyte consists of a solution of lead fluosilicate, tin fluosilicate and free hydrofluosilicic acid. Its composition is maintained between the following limits: Pb, 25 and 35 grams per liter; Sn, 30 and 45; free H_2SiF_6, 60 and 70; total acid, 130 and 150; and specific gravity, between 1.18 and 1.20. Originally this electrolyte is prepared by dissolving litharge in cold H_2SiF_6. This operation must be kept at a temperature below 80° F., in order to prevent the dissociation of the acid with the formation of PbF_2 and SiO_2.

This acidified $PbSiF_6$ solution is subjected to electrolysis with high-tin anodes to build up the tin content to the point desired. The free acid content of the electrolyte must be checked periodically, because an insufficient amount of free H_2SiF_6 causes hydrolization of $SnSiF_6$, producing insoluble basic tin fluosilicate, $SnSiF_6.4Sn(OH)_2$, which precipitates and drops to the bottom of the tank. Hydrofluosilicic acid is not only lost by this hydrolysis, but tin is also removed from the electrolyte. With a low free acid content in the electrolyte, a white precipitate forms very readily in the tanks, which on one occasion contained: Sn, 61.96 per cent; SiF_6, 16.7; F, 2.33; Pb, nil. During the formation of this precipitate, the free acid content of the electrolyte was down to 45 grams per liter, while the tin content was 53 grams per liter.

In regular operations, the electrolyte is continuously circulated through the electrolytic tanks, entering at the top and leaving at the bottom by means of a shield, which carries the solution to an overflow at the top of the tank. The solution flows to a central tank equipped with steam coils, where it is heated to 105°F., the temperature maintained in the depositing tanks.

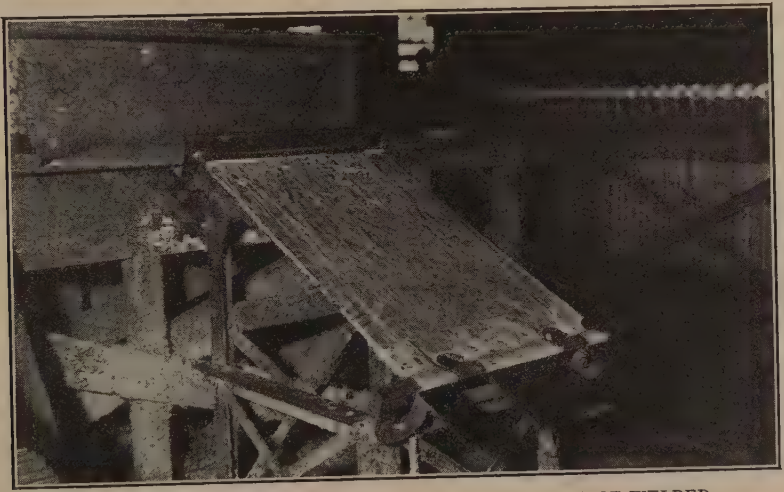


FIG. 2.—STARTING-SHEET PLATE, JUST CAST AND SPOT-WELDED.

During electrolysis, small amounts of iron, nickel and zinc, which stand above lead and tin in the electromotive series, are continuously being dissolved from the anodes, and gradually accumulate in the electrolyte in appreciable quantities, replacing an equivalent of tin and lead. As the decomposition voltages of these fluosilicates are above the operating voltage of the tanks they do not deposit cathodically. Circulating the solution through a tank containing solder shot apparently checks the accumulation of these impurities. This tank is placed between the regular depositing tanks and heating tank. Although this practice cannot be explained theoretically, it has been found to be a simple method of keeping the electrolyte in good condition.

The electrolyte is sampled and tested daily, and free H_2SiF_6 is added as required. If the lead-tin content of the electrolyte becomes too high, two liberator tanks, equipped with insoluble carbon anodes, are cut into the electrolytic circuit.

Addition agents are regularly added to the electrolyte, to cause a smooth, hard, dense deposit of lead-tin to form, the quantity necessary varying with conditions. Glue has been found very satisfactory for this purpose.

Tank Operations.—There are 36 electrolytic depositing tanks, each holding 31 anodes and 32 cathodes. The anodes are spaced about 4½ in. center to center, and the cathodes inserted between, as usual. Individual electrodes in each tank are connected in multiple, and electrically the tanks are so arranged that pairs of two are connected in series, and these pairs are also connected in series. The tanks are made of concrete and lined with a pitch and mastic mixture about ⅜ in. thick. The tank dimensions are 11 ft. 6 in. long, 2 ft. 6 in. wide and 3 ft. 9 in. deep.

Usually the electrolysis is conducted at 15 amp. per sq. ft. of cathode area with an average voltage drop of about 0.34 volts between electrodes. The current efficiency under these conditions varies between 90 and 96 per cent, averaging about 93 per cent over a period of time. The amount of solder deposited per tank day varies with the composition of the anodes and the kind of impurities present. Owing to the difference in the electrochemical equivalents of tin and lead, the higher the tin content of the anode with the same impurities, the lower the weight of solder deposited with the same consumption of electric energy.

In regular operations 30 tanks are usually operating, while residual slimes are being removed from the other six or electrodes are being changed.

In electrolytic refining, there is a first-run period of five days, after which the cathodes are removed, washed and transferred to the melting kettle. The anodes are also removed and cleared of adhering slimes, because a thick layer of slimes has the effect of a diaphragm and greatly increases the voltage drop on the tanks. The anodes are returned to the tanks and new cathode starting sheets are inserted. After another five-day period of deposition, the cathodes and anodes are removed as before, but this time the anodes, after cleaning, are returned to the anode kettle to be remelted and cast into new anodes together with unrefined metal coming into the cycle for electrolysis. Anode scrap amounts to about 25 per cent of the original weight of the anodes.

In cleaning the residual slimes from the anodes, the latter are placed in a tank where slimes are removed by scraping and given a first washing with acidified (H_2SiF_6) water. The slimes are then filtered and washed in a Shriver press, and held for further treatment. The amount of slimes varies with the impurities present, but it may be safely assumed that for each per cent of impurities in the anodes, about 2 per cent of slimes will be formed. Of course, the analysis of slimes also varies with the compositions of the anodes.

The cathodes, after being washed, are placed in a 60-ton kettle and melted. In electrolysis no attempt is made to produce a cathode of definite composition, therefore after melting the metal is handled in one of two ways, as circumstances dictate at the time. It may be cast directly into 60-lb. pigs, sampled, assayed and held as a master lot to be used for blending in making up smaller orders; or it may be sampled in the kettle and held molten until assays are obtained and then be brought to a definite composition with Straits tin or virgin lead, after which it may be cast and used for an immediate order or held for future smaller orders. In any event, the cathode analysis is not definitely controlled but rather allowed to wander with the input of anodes, and then blended with virgin tin and/or lead to produce specification solders in such commercial shapes as are desired.

The Solder

Electrolytic solders have been made containing from 10 to 45 per cent tin, and a great number of chemical and spectrographic analyses have been made for impurities. A typical spectrographic analysis is:

Cu, 0.001 per cent; Ag, 0.10 oz. per ton, Bi, 0.003 per cent; Fe, 0.001; Ni, 0.0001; insol., 0.0002; Mg, 0.0001; Si, 0.0001; Ca, 0.0001. The following were not detected: Zn, Al, P, As, Au, Ba, Cd, Cr, Ga, Ge, Hg, Li, Mn, Mo and Na. The antimony content of electrolytic solder averages around 0.02 per cent; but since this is lower than many specifications it is often necessary to add antimony, to fulfill the specification of the purchaser.

The electrolytic solder produced by the United States Metals Refining Co. since 1927 has been sold to the trade for all the purposes for which solder is used. From these commercial applications, as well as from laboratory tests; it has been found to be very uniform in composition and physical characteristics.

The process used by the United States Metals Refining Co. is proected by U. S. Patent 1842028, issued Jan. 19, 1932.

DISCUSSION

(Carle R. Hayward presiding)

H. R. Hanley,* Rolla, Mo.—What is the approximate analysis of the anode slime, and what percentage of the total tin is found in this slime?

M. Heberlein.—This slime contains in the neighborhood of 40 per cent tin. It varies between 40 and 45. Copper is 1.5 to 2 per cent, lead about 10 per cent, antimony in the neighborhood of 15 to 18 per cent, arsenic between 3 and 6. Gold is up to 2½ oz. per ton, and silver is up to 220 or 250 oz. As far as the relative amount of the tin going into the slimes is concerned, it is not more than about 15 to 20 per cent. This is considered high, I have to grant that, but at the most it would be in the neighborhood of 15 per cent.

---

* Missouri School of Mines.

L. S. Deitz,* Tottenville, N. Y.—It has been stated that approximately a total of 10 per cent impurities is an economic limit in the anode. I believe you listed for the average anode something like 2 per cent antimony and 50 oz. of silver. If it is a fair question, is the precious-metal content of these anodes a vital part of the economic picture?

M. Heberlein.—It is a part. It is not the most important question, but it is an incidental question. On the other hand, I regret to state that we are not in the position to go further into detail regarding the slimes.

A. Butts,† Bethlehem, Pa.—In depositing alloys, it is the common experience that variation in the current density will favor the deposition of either one metal or another. I wonder if that is true in this case.

M. Heberlein.—It is always true in depositing lead and tin, and we have found by maintaining a temperature of slightly above 100° F., and by maintaining the analysis, as we mentioned in the paper, that the tin deposit is favored. The more valuable metal of the two, which is tin, is favored.

A. Butts.—By raising the current density?

M. Heberlein.—No, by maintaining the current density of 15 amp. per square foot.

A. Butts.—How about raising the current density? Does more tin come out or less?

M. Heberlein.—We have found very little variation by raising the current density.

E. F. Kern,‡ New York, N. Y.—I have had to do with the electrolytic refining of lead from the time that it was first carried out in the laboratory in a beaker. Even then, when a lead anode that contained apparently no tin was used, the tin was found going over on the lead cathode; in fact, any amount of tin from a trace up to as high as 60 per cent dissolved along with the lead, and both were codeposited on the cathode, as there is a very small difference in the electrode electromotive force of lead and tin in fluosilicate or fluoborate electrolytes—about 0.02 volt.

In an acid solution of fluosilicate, fluoborate, perchlorate, and complex acids of these types, tin and lead will dissolve simultaneously and will codeposit as an alloy on the cathode, and the metal impurities that are lower than lead and tin in the electromotive series remain in the metallic state as anode residues.

Formerly, in the electrolytic refining of lead, when a small amount of tin was deposited with the lead cathode, it could be readily removed by steaming or poling, the tin being oxidized along with a proportionate amount of lead, producing a lead-tin oxide mixture from which solder alloy could be readily produced by first reducing a relative part of the lead oxide, using a calculated amount of carbon and afterwards reducing the remaining lead oxide and the tin oxide together by the usual reduction method of melting, producing as high as 50 per cent lead-tin solder.

---

* Nassau Smelting and Refining Co.

† Assistant Professor of Metallurgy, Lehigh University.

‡ Professor of Nonferrous Metallurgy and Electrometallurgy, School of Mines, Columbia University.

Ordinarily, the lead-tin oxides produced by steaming or poling the molten cathodes is very pure tin-lead oxide, and gives a pure solder when reduced. Neither anode nor cathode current density has any apparent effect upon the simultaneous dissolving of lead-tin anodes and their codeposition on the cathodes. Current density, however, does control the physical character of the deposited lead-tin cathode. The most satisfactory current densities is from 10 to 15 amp. per square foot of electrode surface.

M. W. Krejci,* Worcester, N. Y.—In the removing of the copper from the solder, is sulphur used?

M. Heberlein.—Yes.

M. W. Krejci.—Is that not probably the cause of the high tin in the slimes, owing to the formation of the stannites, so that it is difficult to get all the sulphur out of the solder?

M. Heberlein.—The final copper is removed by a treatment with sulphur, but we have the stannites already present before the sulphur treatment, and the metal itself is always cleaned after the sulphur treatment, so that the metal contains practically no sulphur.

K. Dengg,† Kearny, N. J.—Is the age-hardening property affected in electrolytically formed metal; either this lead-tin solder or, say, lead-antimony metal—metal that still has this intermetallic compound like arsenide of copper?

M. Heberlein.—I am afraid I cannot answer that question.

K. Dengg.—I ask that because in certain industries, like the storage-battery industries, it is possible to cast grids only two or three days ahead. If something could be done in this direction as indicated, probably we could keep them for three weeks in a bin and from that bin draw what we wanted.

Here is another thing that joins in. In the days when we used 7 per cent antimony lead, the age-hardening could go on gradually, but owing to the mechanization of the grid casting, which now all large companies have accomplished, at least a 9 per cent metal must be used, otherwise distortion occurs in the next operation, in pasting, and so generally 9 per cent, 10 or even 11 per cent is used. Exide uses 10, 11 and sometimes 12 per cent Sb, some of the others use 9, and we happen to use 9 per cent.

M. Heberlein.—I may be able to answer this question indirectly. We have conducted experiments along these lines by shipping old and newly refined solder with the object of obtaining the reaction of the consumers. The indications are that the age has no effect on the workability or quality of the electrolytically produced solder.

C. E. Swartz,‡ Cleveland, Ohio.—The upper limit of tin content in the solder is 45 per cent. Being interested in very much higher tin content of alloys, and alloys that are essentially lead-free—that is, containing much less than 0.25 per cent, perhaps of the order of 0.05 per cent, lead, I should like to ask whether any thought has been given to the application of this process in refining of alloys containing, say,

---

* Metallurgist.

† Thomas A. Edison Co.

‡ The Cleveland Graphite Bronze Co.

90 per cent tin or thereabouts, with reference particularly to the removal of iron from these alloys.

Inasmuch as this country is a large user of tin—the largest user in the world, in fact—too little attention has been paid to the refining of tin alloys and various kinds of tin scrap containing very small amounts of impurities such as iron and lead.

The processes as carried out in all plants with which I am familiar were extremely crude and time-consuming, and very often unsatisfactory, and some such process might have application in the refining of these higher tin alloys.

M. Heberlein.—We were not attempting to make a solder with a higher tin content. We were interested in producing a high-grade commercial solder, so this problem has never been attacked from that angle.

E. F. Kern.—The electrolytic refining of tin was formerly carried out by the American Smelting & Refining Co. at Maurer, N. J., and quite successfully done. Dr. Linville did considerable work on the electrolytic refining of tin, and he probably can tell you that tin was produced of a high percentage of purity. Electrolytic refining of tin was discontinued because there is really no demand for tin of over 99 per cent purity. If there should be a demand for tin of 99.9+ per cent purity it can be produced by a similar method, as described by Hermsdorf and Heberlein.

As far as the fluosilicate and the fluoborate electrolytes are concerned if you carry out the refining of tin-lead alloys of any amounts of each metal together, you will find that the cathode will contain the two metals in amounts relative to the composition of the anodes. There is no difference at all, whether fluosilicate or fluoborate electrolyte is used. It happens that fluosilicate is the cheaper electrolyte.

K. Dengg.—How often is it necessary to wash the slime from the anodes?

M. Heberlein.—We remove the slimes every five days. There are two five-day cycles for each set of anodes. The first cycle is operated with new anodes and at the end of this period the anodes are removed for scraping and washing. The cleaned anodes are then placed in the tank with new cathode starting sheets for the second five-day cycle. At the end of the second five-day cycle the whole tank is thoroughly cleaned out. Very little, if any, slime has to be removed from the bottom of the tanks.

Modern Automatic Baghouses for Collection of Lead-furnace Fumes

By R. L. Hallows* and B. M. O'Harra,† Members A.I.M.E.

The term "modern automatic baghouses" as used in the title of this paper is intended to designate a general type of mechanical fume filter, introduced some 20 years ago and gradually improved since that time. It is characterized by its small filtering bags, enclosed in groups of 15 to 30 in steel compartments, and by its frequency of shaking, as compared to the old type of baghouse, which uses much larger bags, shaken at much longer intervals. Automatic baghouses are produced by a number of well-known manufacturers.

Some recently constructed baghouses of the old type have embodied some of the principles of the automatic type, in that they are divided into several compartments, with separate fans for the different compartments, and flue headers arranged so that when the fan to any one compartment is shut down preparatory to shaking the bags in that compartment, the bags are put under suction by the draft from the other fans, thus making possible more efficient cleaning of the bags. These baghouses have motor-driven shaking mechanisms, and generally are operated under higher pressure and shaken at more frequent intervals than was the practice with the old style baghouse, and consequently have greater filtering capacity per unit of bag area. It is possible to interconnect the fan motors and the motors driving the bag-shaking mechanism, with suitable relays and timing devices, so that the operation of this type of baghouse also becomes to a considerable extent automatic.

These baghouses are intermediate between the old style of baghouses, strictly speaking, and the completely automatic baghouses. They may be considered just as modern as the latter, and their proponents can no doubt cite many advantages for them. The authors are less familiar with them than with other types, and the following discussion will be limited to a comparison of the automatic baghouses and old style baghouses, with particular reference to the experience of The Eagle-Picher Lead Co. and The Eagle-Picher Mining and Smelting Company.

Manuscript received at the office of the Institute Aug. 22, 1936.

* Manager Lead Smelter of The Eagle-Picher Mining & Smelting Co., Galena, Kansas.

† Metallurgist, The Eagle-Picher Mining & Smelting Co.

Old and New Types

The old type of baghouse usually contains many hundreds of bags, which usually are about 30 ft. long and 18 in. in diameter. These bags are hung inside a brick building on pipes or shafting, which are actuated by means of cams or eccentrics to shake the bags hung therefrom. The usual practice is to shake the bags at intervals 2 to 12 hr. apart. This bagroom invariably is on the pressure side of the suction fan, and usually from 1 to 3 sq. ft. of filtering surface is required for each cubic foot of gas per minute that is handled.

The modern automatic filter takes the dust-laden air, or fume, into hoppers below the compartments, over which are thimbles to which filtering bags are attached. The fume then travels upward into filter bags where the solids are deposited on the inside of the bag and the clean gas drawn through the fabric to the outlet manifold and thence through the fan to the stack, the baghouse thus being on the suction side of the fan.

The bags are cleaned usually every few minutes. A timer controls the shaking frequency and it can be adjusted to make the shaking interval from 2 min. to 1 hr. Compressed air, controlled by the timer, is used for the operation of the shaking mechanism, which consists of a piston and rod to which the bags are fastened by a ring. The air also causes a valve to close, which cuts off the compartment to be cleaned from the circuit. Immediately, air is introduced from the outside through the filter cloth in the reverse direction. One compartment at a time is cleaned. The period of shaking or cleaning usually varies between 2 and 10 sec. The fume collected drops into the hoppers below the bags and ordinarily is removed continuously or at frequent intervals by means of screws or similar conveyors.

Advantages of Modern Baghouse

Ordinarily, the bags used for filtering are about 8 in. in diameter and 10 ft. long, made of cloth of finer weave than is used in the old-style larger bag. Good practice for the modern baghouse calls for only 1 sq. ft. of filter cloth to handle from 3 to 8 cu. ft. of gas per minute. Thus, the filtering area in the modern baghouse may be as little as one-tenth of the area used in the old type for handling the same volume and dust concentration. This feature, perhaps, is the most striking difference between the old and the new types and probably is the greatest single advantage of the new type.

Other advantages claimed for the modern automatic baghouse include greater cleanliness and consequently less hazard to health, and uniform draft conditions due to the frequency of cleaning the bags; whereas in the old bagroom the resistance increases as the layer of dust on the bags increases in thickness and as a consequence the draft or volume handled decreases. Also, leaks may be repaired in the modern type more conveniently than in the old type, and the danger of fire destroying the whole bag hanging or many bags is lessened.

The Eagle-Picher Lead Co. and its subsidiaries operate both old-type and new-type bagrooms, and wherever a modern bagroom is operating an old type also is operating, or has operated, for almost exactly similar service. Thus some comparisons can be drawn:

At East St. Louis, the fume from one Newnam ore hearth (Scotch hearth) is handled by a modern 10-compartment automatic filter, which has a total cloth surface of 4360 sq. ft. At Galena, Kansas, the fume from each ore hearth requires one room of the old-fashioned baghouse, containing 176 bags having a total of 26,400 sq. ft. of filtering surface. The dust load and volumes of gases handled at East St. Louis are comparable to those at Galena, so the old-type bagroom has six times as much filtering area as the new type for the same service.

Another comparison may be made on collecting basic lead sulphate pigment. Formerly, this product was made at Joplin, Mo., and collected in the old-type baghouse containing 540 bags having an area of 81,000 sq. ft. of surface. At Galena, this product is made and collected in a modern 10-compartment automatic filter having 250 bags and 5365 sq. ft. of filtering surface. In this instance, some 15 times as much area was provided in the old bagroom as is necessary in the new type.

A third comparison may be made on the collection of fume from blast furnaces. Formerly, a blast furnace was operated at Joplin and the fume was collected in an old-fashioned bagroom containing 768 bags having a filtering surface of 115,200 sq. ft. The fume from a blast furnace now operating at Galena under similar conditions is collected in a 24-compartment modern automatic filter containing 432 bags having a total surface of 8250 sq. ft. Here 14 times as much filtering area was provided in the old baghouse as in the automatic one.

LIFE AND COST OF BAGS

In addition to the blast-furnace fume, the baghouse at Galena handles the fume from a reverberatory furnace smelting battery scrap. It cannot handle the fume from both furnaces at the same time, but the two furnaces are operated alternately, thus making possible a comparison of the baghouse performance on two different kinds of fume. A much longer life is obtained from the bags when the blast furnace operates than when the battery-scrap reverberatory operates. This is explained by the high sulphur trioxide concentration of the battery-scrap gas, which has a marked deteriorating effect on the woolen bags. Ordinarily, the same temperature conditions should prevail in the modern automatic bagroom as in the old-fashioned one, 210° F. maximum for cotton bags and 250° F. for woolen bags. It is usually the practice in the automatic baghouses to have a damper immediately ahead of the inlet manifold which is automatically opened and closed by thermostatic control, allowing outside air to be introduced for cooling.

Mohair filter cloth, 24 threads per inch and weighing 12 oz. per sq. yd. is used at Galena in the old-type baghouse. Fine, fleecy, white woolen cloth, weighing 12 oz. per sq. yd. and having some 30 to 40 threads per inch, is used in the automatic filters.

A woolen bag, 8 in. in diameter and 10 ft. long, for the automatic filters costs about $3.40 at the present time, or 16¢ per sq. ft. of filtering area. A seamless bag, 18 in. in diameter and 30 ft. long, for the old-type bagroom costs about $15, or 10¢ per sq. ft. of filtering area at the present time. If we assume that 1 sq. ft. of filtering area in the new bagroom is equivalent to 6 sq. ft. in the old-fashioned type, the cost comparison becomes, on a volume-handled basis, 16¢ and 60¢, or roughly, a cost of four times as much for the larger bags. While the initial cost of the bag equipment in an automatic filter to handle a given gas volume may be but one-fourth that of the old-style baghouse, it does not necessarily follow that maintenance or bag replacement will be of the same order.

At Galena the life of a bag in one of the automatic filters is about three months. The life of a bag in the old baghouses for similar service is two or more years, so the cost of bag replacement is considerably in favor of the old type.

At East St. Louis, where a mechanical filter is operating on fume from battery-scrap furnacing, cotton bags are used. That plant has found that while wool gives considerably longer life, the difference in price in favor of cotton makes the latter more economical in spite of more frequent replacements. A life of a week or two is obtained from the cotton bags. Their cost is in the neighborhood of 50¢ each. A bag at East St. Louis measures 100 in. in length and 8 in. in diameter.

Operating Details

Very little trouble or expense has ever been experienced in keeping the mechanism functioning properly in the new-type filters. One man, who also has other duties, is on each shift for each of the mechanical filters. He takes care of oiling, inspection and bag replacements. At one of the filters, the fume that is collected is removed from the hoppers beneath the bags by screws which convey the material to a pug mill. The bagroom attendant looks after this pugging operation, which is done periodically.

The automatic filter on basic sulphate white lead at Galena is handling about 25 tons per day and filtering about 20,000 cu. ft. of gases at 210° F. per minute. These conditions correspond to 0.8 gram of solids per cubic foot. The shaking cycle for this filter is 3 min. and 40 sec. The period of shaking is 7 sec. As 5365 sq. ft. of filtering surface has been provided, this corresponds to approximately 3.7 cu. ft. of gas per minute per square foot of filtering surface.

The other mechanical filter at Galena, made by a different manufacturer, operates on a shaking cycle of 2 min. and 15 sec. The shaking period is 4 sec. Some 20 tons of solids have been filtered in this unit per day. The volume handled is about 40,000 cu. ft. per minute at 210° F. This corresponds to 0.3 gram of dust per cubic foot. This filter has a total filtering surface of 8250 sq. ft. Thus, approximately 4.8 cu. ft. of gas per minute is being handled by 1 sq. ft. of filter cloth.

Very few, if any, of the large lead smelters are using automatic baghouses for collecting blast-furnace or roaster fume. Cottrells or old-fashioned baghouses are being used. Possibly one reason for this is that few major lead-smelter baghouse installations have been made in recent years since the modern automatic baghouse reached its present state of development.

The 10-compartment automatic filter at Galena was purchased and erected in 1932. The complete cost of foundations, building and filter was $10,721. The building consisted of little more than siding and roofing the structural steel supporting the filter. Probably the replacement cost at the present time would be one-fourth or more greater.

Collection of Lead and Zinc Dusts and Fumes by the Cottrell Process

By Harry V. Welch,* Member A.I.M.E.

Early in the development of the art of metallurgy, it was noted that a distinct difference existed in the character, collection possibility and health hazard of the "smoke" from lead furnaces and those from copper plants. Zinc-plant fumes, although not so detrimental to health, were closely allied in nature to those of the lead works. In Cottrell plants, there are sufficiently distinct differences in operation and amount of construction between those for lead and copper to justify their consideration under separate headings; therefore, while the application of the process at copper-reduction works was covered by the writer some two years ago in the Transactions[1],† this discussion will confine itself more distinctly to "fume" collection. General information on the process has been presented in numerous articles and by many authors: Cottrell[2], Schmidt[3], Bradley[4], Anderson[5], Labbe[6], Shiga[7], Rathbun[8].

"Fume" may be defined as material, metal or nonmetal, elemental or compound, evolved as a vapor from a furnacing or chemical reaction and condensing, chilling or reacting within the gas stream to yield a solid form, and in this definition liquid particles are solids in a sense as distinguished from gases or vapors. Such condensed particles are of minute form, on the order of "smoke," and, for example, on the order of a few hundredths of 1 micron (1 micron = 1/25,000 in.) to perhaps 3 microns, with agglomerates, in relatively small proportions of many particles.

Metallurgically typical fume products are lead compounds, oxides, carbonates and sulphates; elemental zinc, more commonly encountered as a fume particle of zinc metal with a surrounding "skin" of zinc oxide; arsenic, both metal and oxide and some of its more complex salts such as added sulphates as found in flue dusts; antimony, more particularly its oxide forms; and elemental sulphur, sometimes a troublesome product in Dwight-Lloyd sintering-plant fumes. These products, particularly the elemental or lower oxide forms, have relatively appreciable vapor pressures at the existing operating temperatures as reported by Welch and Duschak[9], Ingold[10], Johnston[11], Millar[12,13].

Manuscript received at the office of the Institute Aug. 17, 1936.

* Chief Chemist, Western Precipitation Company, Los Angeles, Calif.

† References are at the end of the paper.

HISTORICAL

As mentioned above, it was early observed that products escaping from lead reduction were much more difficult to collect and in general were of greater magnitude than those from copper plants. However, the simple lead carbonate ores then smelted produced gases less acid than those common at copper works, and crude forms of baghouses came into use. Development of the baghouse for neutral or only slightly acid gases progressed steadily, and today many are in use involving much ingenuity in their mechanical construction, and practically of completely automatic operation, involving thousands of bags and tens of thousands of square feet of bag surface. As their construction and operation is not a part of this paper, the reader is referred to other contributors to this volume and to the previous literature: Eilers[14], Alexander[15], Austin[16] and Cregan[17].

The acid gases commonly present from Dwight-Lloyd sintering machines rapidly deteriorate the bags unless the acidity is neutralized by hydrated lime dust or its equivalent introduced into the gas stream before its entrance to the bags. With few exceptions, collection is made today in Cottrell precipitators. Often blast-furnace gases are joined with the Dwight-Lloyd gases. There are many such plants in operation and an essential requirement in such installations is a recognition of the basic requirement that such gas and its content of suspended solids be "conditioned." Later paragraphs will give more detailed discussion on means and theory of this particular problem in Cottrell operation with basic dusts. It was the lack of understanding of this problem, together with the inadequacy of high-voltage electrical equipment then available, that led to the failure of the truly pioneer and first commercial plant attempted in the year 1885.

Previous to 1878 the highest potential available for use by man was that effected by the discharge of a Leyden jar. As early as 1824 a precipitation of smoke particles on the walls of a smoke-filled bottle was caused by a charged Leyden jar connected with the bottle by means of a wire through its cork. Since no practical or theoretical advantage suggested itself, the discovery was soon forgotten, to be discovered again about a quarter of a century later, in 1850, and forgotten, and rediscovered once more in 1884 by Sir Oliver Lodge. The third discovery fell in with the newer developments in science, particularly the invention of the Wimshurst machine in 1878, by means of which high-voltage direct current could be generated. Practical installation protected by patent application (Walker[18]) was made in 1885 at the Dee Bank Lead Works in North Wales[19].

The "precipitator" consisted of a number of sharp-pointed wires projecting into the flue and connected to a Wimshurst machine of two

5-ft. dia. glass plates driven by a 1-hp. steam engine. As real electrical precipitation of such material required gas and deposit conditioning, and a system of collecting electrodes as well as discharge electrodes, and a sensible delivery of power, and as under test a Wimshurst of even larger plate area was insufficient to energize a section of 6-in. pipe 6 in. long, it is evident that the plant failure was due to factors not known at that time.

During the period intervening between this first unsuccessful attempt at electrical precipitation in 1885 and the first truly successful commercial unit of Cottrell design in 1908, the electromagnetic generation of electric power developed from Faraday's copper disk and horseshoe magnet and became a great industry, and Cottrell, therefore, had at his command vastly greater supplies of electrical energy than the earlier investigators. It is interesting to observe that within the staff organization of lead reduction works of a half century ago, progressiveness of thought and action were keen enough to provide the facilities for the first, as we look upon it now, feeble commercial attempt, and that a quarter of a century later on the Pacific Coast the first really successful commercial installation was made.

This first successful commercial installation at a lead smelter referred to a special problem of refinery operation rather than to the usual lead-plant fume collection from furnace gases, but it is of interest historically. The Selby smelter (Fig. 1) is at Vallejo Junction, on the east side of San Francisco Bay. Its metallurgical operations include the refining of bullion, and the usual parting kettles are in use for the separation of silver from gold. Fumes from the parting kettles originally passed to an individual stack and at times the escaping sulphuric acid mist was exceedingly troublesome. Up to the time of Cottrell's work, there was no simple satisfactory and practical method of collecting sulphuric acid mist, and Cottrell's process having by that time been described and discussed in press and journals, his assistance was sought on the control of the acid mist discharge from the stack from the parting kettles.

The design of this precipitation unit was limited by the potential obtainable from available power transformers—about 25,000 volts. Spacing between discharge and collecting electrode was therefore limited to 2 in. (4 in. center to center of collecting or grounded electrodes) and the discharge electrode was of the many-point type secured by strips of serrated mica placed and held between two half-round strips of lead. The precipitator consists of two units, each of two sections in series. Each section contains 12 rows of collecting or grounded electrodes, each row comprising four strips of 4-in. by 4-ft. lead supported at the top and separated by 4 in. between strips. In effect, it is a plate 3 ft. 2 in. by 4 ft. with half its area in equal proportions cut out as four full-length vertical strips. Opposite the middle line of each pair of collecting electrodes is the discharge electrode of serrated mica and supporting lead.

The original "pubescent" electrode of Cottrell's early work incorporated asbestos fiber either as a fibrous string winding about a wire or rod or as a thin layer between two wires twisted for binding and stiffness. Serrated mica strips were early substituted for the asbestos fiber as being more resistant to acid attack and of added reliability and structural strength. It was evident early in the development that this type of "pubescent" or its near equivalent of the somewhat mechanically stronger serrated-mica discharge electrode constituted a serious limitation on the application of the process. The necessity for a radius of curvature small enough to secure a corona discharge for the spacing and voltage applied, however, was always present. Encountering the problem of high temperatures of cement-kiln gases, of upwards of a million cubic feet of gas per minute to be "treated" and limitation of space and expenditure, Schmidt[20] discovered that the practical solution to his problem and to the art lay in using much higher potential differences, greater spacing and round, plain wires. For example, voltages from 50,000 to 100,000 volts, spacing between discharge and collecting electrodes of 3 to 6 in., and discharge electrodes of wire from No. 8 size down to very fine wire.

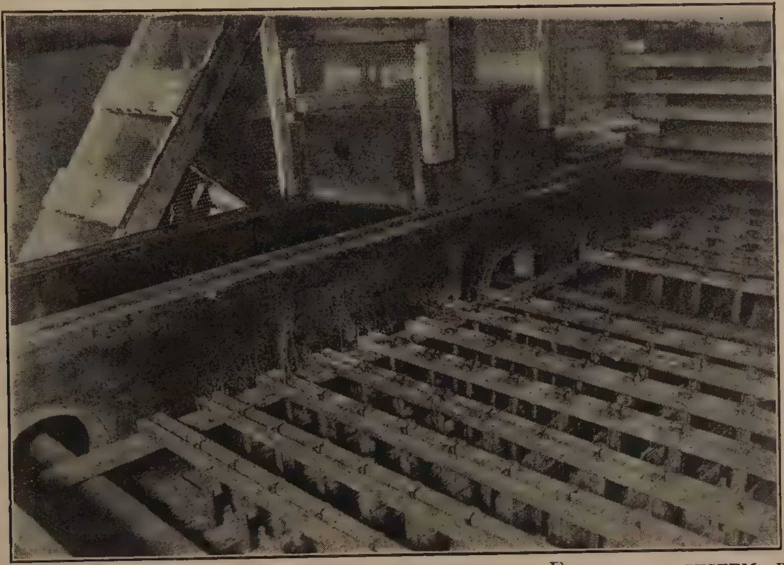


FIG. 1.—SELBY SMELTER, ACID-MIST PRECIPITATOR. ELECTRODE SYSTEM WITH COVER REMOVED.

ELECTRODE DEPOSITS

The picture of electrical precipitation is a simple one: that of a discharge electrode (commonly negative) with a very small radius of curvature (a wire) and a collecting, positive or grounded electrode (a plate or pipe), between which two electrodes gases carrying suspended solids are made to pass, precipitation of the suspended solids upon the collecting electrode taking place upon the establishment of suitable unidirectional, high-potential electric field between the electrodes. The relationship of distance between the electrodes, radius of curvature of the discharge (negative) electrode and voltage applied must be such as to provide a constant bluish electric discharge or a corona glow from the discharge electrode. In theory, the corona glow indicates potential gradient at the surface of the wire sufficient in intensity to disrupt the uncharged gas molecules, causing a positive charge to enter the metal electrode and the negative electrons to attach themselves to gas particles and then moving under the influence of the static field in the direction of the electrode of opposite polarity, or the positive or collecting electrode. These charged gas particles come into contact with suspended solid particles and thereby the latter are charged and begin their movement toward the collecting electrode. Upon arrival at the collecting electrode the charged dust particles should yield their charge to the electrode and become grounded—adhere to and to all intents and purposes become a part of that electrode. It is evident, however, that should the deposited dust particles fail to lose their charge, further precipitation would shortly become impossible and the suspended solids would then pass through the electric field without precipitation being effected. This is an extreme case and, while obtainable in the laboratory with zinc oxide fume in dry gases and dry deposit, for example, is practically never found in actual commercial plant operation. It is distinguished in test-plant operation from the beginning of a test with clean electrodes and as indicated on primary instruments of decreasing ampere flow, increasing potential and visibility of stack loss. The effect is that of a deposit of a sheet of continuous dielectric upon the collecting electrode. It is probably true that such a deposit is not in reality a perfect dielectric and that with refinement of precision in test, some grounding of deposited particles could be continuously detected. It is stated as a "practical observation."

The more usual phenomenon is a deposit showing characteristics of a discontinuous dielectric, also termed a porous dielectric, and more commonly called "poorly conducting deposits." Ordinarily these are basic in nature and zinc-plant and lead-plant fumes are good and sufficient examples.

In this type of porous dielectric deposit, and where it has not been "conditioned" (made conductive), the electrical phenomena are sharply at variance with the case above of a continuous dielectric. Starting with a clean precipitator and a suspended solid in the gases, which upon precipitation becomes a porous or discontinuous dielectric, the instruments on the primary circuit will show, as the test proceeds, a continually decreasing voltage and increasing amperage to a given limit as fixed by the characteristics of the electrical set with a corresponding decrease in collection efficiency from near 100 per cent to near zero. It is obvious that removal of the deposit, or the major portion of it, for example, by rapping the collecting electrode, would again restore the operation to its original starting or near its starting position (dependent on the amount removed) and that such cycles and continued precipitation could be maintained indefinitely. Thus, the conditioning of poorly conducting deposits is a practical problem of minimum plant size, maximum plant "treating" capacity and lowered investment; a factor change of degree and not of physical state.

Explanation and theory are as follows: At the start ionization and the resultant charging of gas and dust particles are confined to the wire or rod electrode, the negative electrode. As the deposit builds up on the collecting or positive electrode and as a porous mass of dielectric particles, there is a corresponding building up of electric field intensity at the "pores" or interstices of the particles until intensity or potential gradient is sufficient to rupture electrically the gas layer within the "pore," giving thereby an ionizing effect and the usual visible glow. This discharge from a surface deposit on the collecting electrode is commonly termed "reverse discharge" or "back ionization," and since its charging effect is positive the precipitation effect is neutralized. Correction of this condition is accomplished by rendering the deposited dust electrically conductive. It is well known that many condensed fumes associate with themselves definite amounts of condensed gases and apparently this condensed gas exists as an envelope about the fume particle. Sulphuric acid mist in its smaller particles is an excellent illustration, since such fine particles may readily be drawn through several alkali wash bottles without absorption, although acid and alkali in actual particle contact react vigorously. In lead-plant and zinc-plant fumes, it is undoubtedly this envelope or effect of condensed gas that gives to the collected fume the character of a semidielectric. The corrective factor, therefore, would be indicated as that which would destroy this dielectric superficial covering of the fine particles and permit their deposit and grounding as a uniform continuous conductive deposit.

Since it was well known that water vapor and water particles exercised a strong influence on high-potential discharge effects, attention was early turned to the consideration of this as a beneficial means. At the same time, studies, largely laboratory, were conducted on many types of dielectric as interposed in a field of high potential discharge[21]. Typical of the effect of lowering of the arcing (sparking) voltage by nonconducting deposits is an example offered by Wolcott[21]. The effect was noted as the decreasing potential that could be maintained between a point (negative) and a plate (positive) as increasing layers of a fume collected from the exit gases of a Dwight-Lloyd sintering machine were added on the surface of the plate. This particular Dwight-Lloyd fume had been found difficult of collection by electrical precipitation and carried an unusually high percentage, 20 per cent of free sulphur. In its dry condition it was sifted through a 100-mesh screen as layers upon the collecting plate and the peak voltage that could be maintained was determined against layer thickness (Table 1).

TABLE 1.—*Thickness of Fume Deposit and Arcing Voltage*

Point Negative and 6 Cm. above Plate

GRAMS PER SQ. FT.	MG. PER SQ. CM.	KV. (PEAK)
0.00	0.00	130
0.85	0.91	120
5.45	5.74	74
8.15	8.78	60
17.75	19.14	50

Since precipitator capacity (gas volume) for a given efficiency is, within limits, proportional to the peak voltage that can be maintained, the seriousness of the lowering of the potential that may be maintained is evident. In the test described, Wolcott found that with the sinter-plant fume the presence of 2.25 per cent moisture in the dust was not sufficient to overcome the lowering of voltage effects while the presence of 2.91 per cent moisture in the product completely grounded the deposit and permitted voltages between point and plate deposit equal to that of a clean plate. Percentage of moisture content varied with the several types of fume, and zinc oxide fume, for example, required but one per cent moisture content to render it conductive.

As illustrative of the relationship of peak voltage and capacity, E. Anderson reports[22] the data secured on a single-pipe test unit (Table 2).

TABLE 2.—*Variation of Tube Capacity*

Cu. Ft. per Min. for 90 Per Cent Efficiency of Peak and R.M.S. Voltages (Maximum Voltages Maintainable, Controlled by Degree of Conductivity of Deposit)

Voltmeter				Capacity in Cu. Ft./Sec. at 90 Per Cent Efficiency	
Sphere Gap[23]		Electrostatic R.M.S.[24]		Per Second	
Kv.	Per Cent	Kv.	Per Cent	Cu Ft.	Per Cent
76	100.0	55	100.0	5.7	100.0
74	97.3	53	96.3	5.4	94.7
66	86.8	49	89.0	4.7	82.4
60	79.0	47	85.4	4.4	77.2
49	64.5	43	78.2	3.2	65.2
40	52 6	35	63.6	2.0	35.2

CONDITIONING GASES AND DEPOSITS

Some investigators found beneficial results from adding steam to the gases, others noted improvement from addition agents to suspended solids such as graphite, carbonaceous products and oil, and for a time there was a lively argument as to whether the requirement for overcoming the adverse effects of basic dust deposits in continued precipitator operation required conditioning of gases or of the deposit. Later work has indicated the value of well conditioned gas, also that conductive gases alone are insufficient for satisfactory precipitation, and that in order to secure sufficient conductivity of the deposited material, the gases as well were always well conditioned.

In a rather rough empirical expression, it may be said that: (1) if a precipitator of a given size is collecting, say, 90 per cent of well conditioned (say 3 to 5 per cent moisture in collected dust) basic fume such as lead-smelter gases; (2) a unit of one-half its size would handle an equal gas volume at the same efficiency on copper-roaster dust (acid gases); (3) that twice its size would be required for gases well conditioned and basic fume not satisfactorily conditioned and (4) something on the order of four times the unit size for well conditioned lead-plant fume, where neither conditioning of gases nor of deposit is provided.

It can be argued, of course, that case 3, conditioning of gases only, cannot exist, and that even though no more moisture in the precipitated dust can be found by usual analytical means with and without water vapor added to a gas of relatively high temperature, nevertheless the mass-action effect could easily place additional and undetectable (by usual laboratory procedure) amounts of moisture on the suspended and precipitated particles. Since the electrical effect of surface creepage on dielectric surface under high potential stresses is striking between a dry and humid atmosphere the consideration is important. While Wolcott[21] in laboratory work found 2.31 per cent moisture insufficient to condition a lead-plant fume containing 20 per cent free sulphur, and 2.91 per cent moisture sufficient to completely discharge the deposit, practical plant operation finds the usual requirements between 3.5 and 5 per cent, with relative humidities occasionally as low as 40 per cent, more commonly on the order of 60 per cent and for especially difficult fumes, such, for example, as contain elemental sulphur, 80 to 90 per cent humidity may be necessary to secure a satisfactory conditioning of deposit.

Since types of precipitator, climatic conditions, day and night operation and characteristics of gases and deposit affect the amount and degree of conditioning required, no precise quantities can be stated. Types of precipitators will receive detailed description in later paragraphs, but it is desired to point out here that the exposed-pipe type requires a minimum of conditioning of gases and deposit, and in areas of abundant rainfall and relative high humidity such as exist in northern Europe many exposed-type precipitators are collecting lead and zinc fume without special conditioning facilities. In the Americas, Australia, South Africa, even this type requires provision for conditioning and commonly the order of requirement may be stated as around 30 per cent relative humidity for exposed-pipe precipitators; 40 to 70 per cent for submerged pipe and plate precipitators; and according to Labbe[6] 80 per cent for the wire precipitator.

Much work was done in early days on all manners of sprays, coarse, fine, high and low pressure, with and without steam, the latter both as addition agent and as atomizing means, but practice now has settled down to a number of sprays each of small delivery and operating at pressures of 250 to 300 lb. Commonly these sprays under 250 lb. pressure deliver approximately ½ gal. of water per minute in the form of a fine misty spray of which about one-half enters the gas stream, partly as vapor and partly as moisture in suspended dust. These sprays are installed in a special chamber where gas velocity is decreased to around 6 or 7 ft. per second and an ample allowance is one spray head to 1000 cu. ft. per minute. Sprays are set on 5 to 10-ft. centers both transverse and longitudinal of the spray chamber, and arranged for control both in groups and individually by a suitable valve system. The number of sprays in operation will vary widely as between winter and summer, day and night, hot and cold furnace tops, stormy periods and dry weather, and so forth.

While general practice, as stated, is with simple high-pressure sprays, a few plants operate with atomizers using low-pressure water supply and effecting atomization by compressed air; these operate in the range of 60 to 90 lb. both for air and water and commonly use about 5 cu. ft. of free air per gallon of water per spray per minute. They are reported to be satisfactory, their special merit arising from the fact that the orifice is much larger than in the simple high-pressure type and therefore is not so easily choked by foreign particles carried in the water stream.

Acid conditioning of gases has also been widely practiced at lead smelters, both alone and as auxiliary to water sprays. Concentrated sulphuric acid mist is a fume and therefore may be present with basic fumes in a relatively dry gas stream without providing the expected conditioning effect. As dilute or moderately concentrated acid fumed into a hot flue is rapidly converted to concentrated acid fume, correction of the undesired condition is not necessarily obtained by acid of lower strength. However, where temperatures are not too high and the gases contain a fair amount of moisture, fumed in sulphuric acid becomes a most effective conditioner. The requirement appears to be on the order of a ton of acid (60° Bé.) to between 5 and 10 tons of Cottrell collection.

Carbon smoke, soot, graphite and various other solid agents have at times been added to improve the conductivity of deposits but although some improvement usually was noted it was not of sufficient magnitude to be worth while in commercial plant operation.

Petroleum in form of a fuel oil has also been used as a conditioning agent and with some success. Oil has a high "wetting" property and appears to neutralize the nonconducting film surrounding or associated with a basic fume particle. It functions best on gases cooled to somewhat below 200° F. by water sprays and requires about 1 lb. per minute of oil spray for a collection of 10 to 20 tons per day of lead-smelter fumes. The cost of oil has prevented its more extended use and it is considered only when water supply is limited and costly.

Acid conditioning of leady fumes by admixture of gases from copper, pyrites or matte roasters before entrance to the Cottrell has also been effective. A special example is the operation of a series plate precipitator at the Tooele plant[25], where excellent capacities at relatively high gas velocities are obtained, and in which sufficient selective precipitation is accomplished to permit the return of collected material from the first two plates to the copper department, and the last two sections to the lead department.

Matte roasting in a multiple-hearth furnace with concurrent movement of gases and charge, and the admixture of this gas to gases from the lead blast furnace and Dwight-Lloyd gases has been utilized with fair success at one or more reduction works.

ELECTRICAL INSULATION

Contending with general plant conditions and operating extended systems of electrodes at 50,000 to 100,000-volt differentials provide a difficult problem in electrical insulation. In the early days of electrical precipitation, insulation between electrode systems was a very serious problem. The porcelain of those days indifferently met the conditions and quartz, marble blocks and marble-block pyramids, firebrick and tile, cement blocks and cement-block stacks all were given a trial at one or more plants. The remarkable improvement in the dielectric qualities of the modern insulator porcelains has placed all other material, except for a few special conditions, entirely out of consideration and the recently constructed plants depend on porcelain both for support insulators and inlet bushings.

On cold, dilute acid gases and where dilution of gases is not permitted, as in the purification installations for contact acid, oil-seal bushings[26] have given excellent service. These consist of an inverted pan or hood attached to the high-potential frame member and at the point where it passes through the top of the shell and with the edges of this pan dipping into a circular oil-filled trough attached to the Cottrell shell, thus providing an oil-seal bushing. Suitable provision is made for renewing the oil and for removing the acid water and sludge which may sink to the bottom of the pan carrying the sealing oil.

Corresponding to the above and for dry plant operation are the "lime seals"[27]. These have been used in special plant construction but have not become widely used although they have much merit in special conditions of operation.

PRECIPITATORS

It was mentioned that the exposed-pipe type of precipitator (Fig. 2) required less conditioning of gases than other types and this is to be accredited to the fact that the tube walls, owing to the cooling effect of the surrounding atmosphere, are at an appreciably lower temperature than the flue gases, and that consequently the deposit on the inner face of the tube, which seldom exceeds ½ in. in thickness, is also of a lower temperature than the gases. Both the deposit and the gases within the interstices of the particle are therefore much nearer dew point than the main gas stream, and are thus conditioned. This type of precipitator has been built with pipe sizes from 5-in. dia. to 12-in. dia. and with tube length from 8 to 17 ft., the longer pipes corresponding to the larger pipe

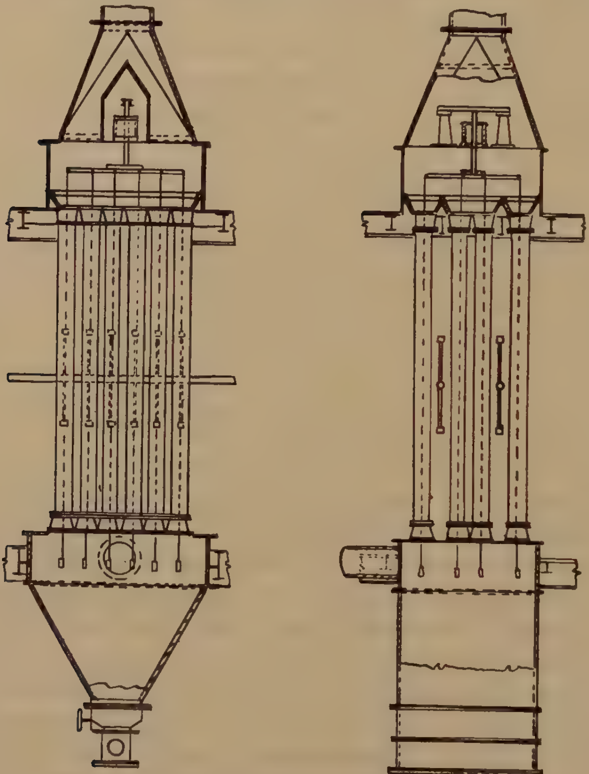


FIG. 2.—EXPOSED-PIPE TYPE OF PRECIPITATOR.

diameters. Gas flow may be either up or down in the tubes, each type of gas flow having certain advantages and disadvantages. Downflow provides more uniform distribution of gases but offers opportunity for once-precipitated dust to escape with the outlet gases. Upflow prevents

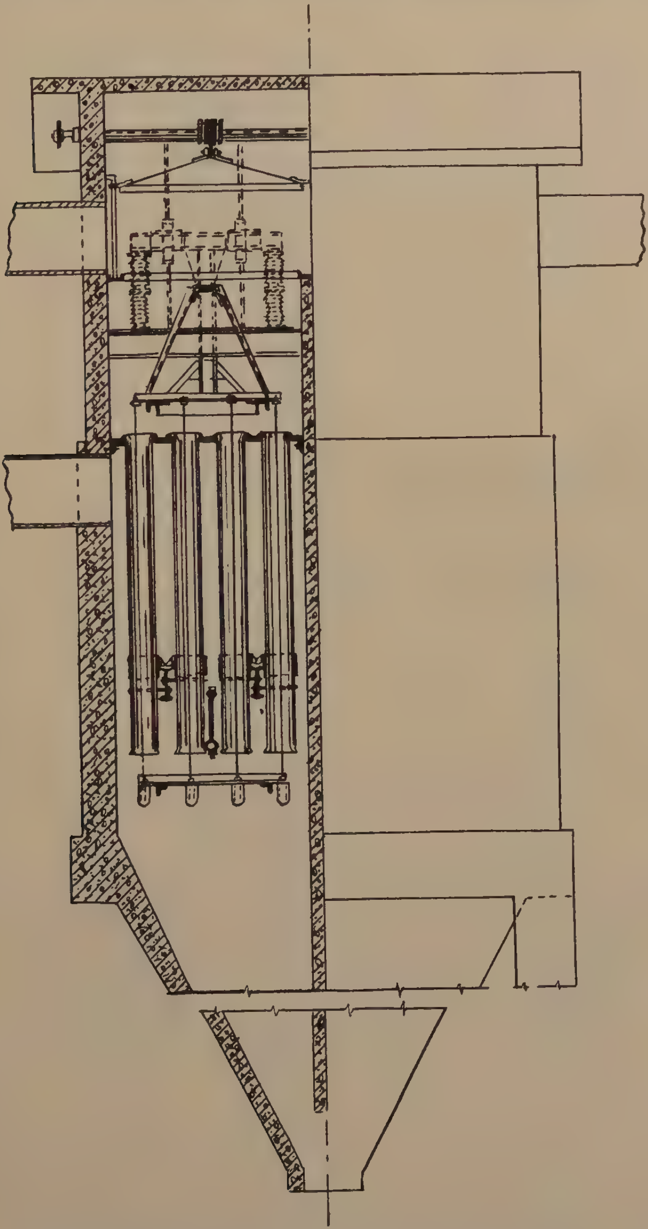


FIG. 3.—SUBMERGED-PIPE TYPE OF PRECIPITATOR.

the loss from carry-over with outlet gases but under low gas velocities in tubes gives trouble in uniform gas distribution. In fact, many plants in Germany and northern Europe have been built with two pipe sections in series, the gases moving down in the first unit and up in the second. These have given satisfaction there, owing to the more humid and commonly cooler weather than obtains in America. Numerous units are operated on lead and zinc-plant gases without conditioning, and this to some extent is offset by additional length of tube and precipitator size.

Unit size may vary from 20 to 30 pipes to 140 or more. Each unit has both inlet and outlet dampers and several units form an installation, which permits taking one unit out of service for cleaning or repairs without serious loss of plant efficiency. A well recognized unfavorable feature of the exposed-pipe type is its susceptibility to corrosion, particularly where additional conditioning of gases is effected by water sprays or acid additions. This arises from the fact that with dependence for the cooling effect on weather conditions, controlled moisture and temperature of deposit is impossible, and actual wetness of walls and deposit provide favorable condition for corrosion.

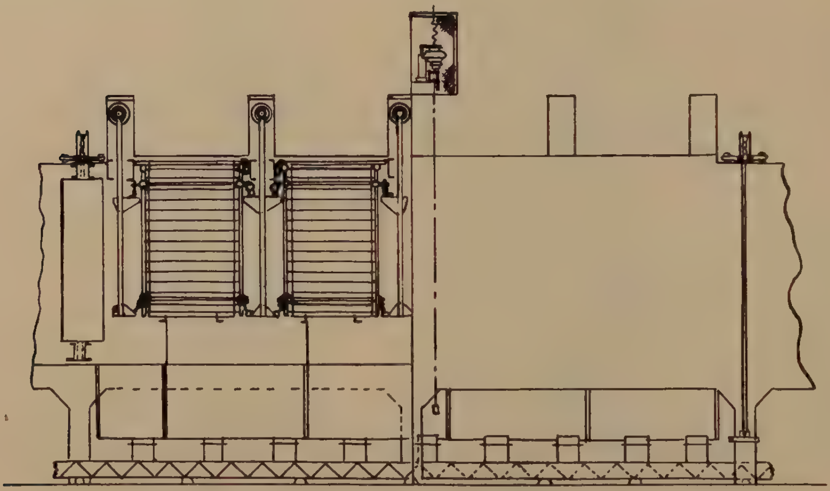


Fig. 4.—Plate type of precipitator.

The submerged pipe unit (Fig. 3) is protected from uncontrolled wall and deposit corrosion because the gases either before or after passing the unit surround and move past the pipes. This added protection is offset to some extent by increased conditioning requirements. It is a very satisfactory type of Cottrell collector and is widely used.

The plate type (Fig. 4) was developed largely as a less expensive form of precipitator than the pipe type and commonly has much less draft loss, ¼ to ½ in. of water-column drop across the precipitator being the usual amount. While this precipitator may be built for gases passing either vertically or longitudinally, the most economical construction is usually the horizontal flow with increased efficiency secured by adding plates in series rather than more units in parallel, as required in the vertical-flow type. This is correct within limits as set by several fac-

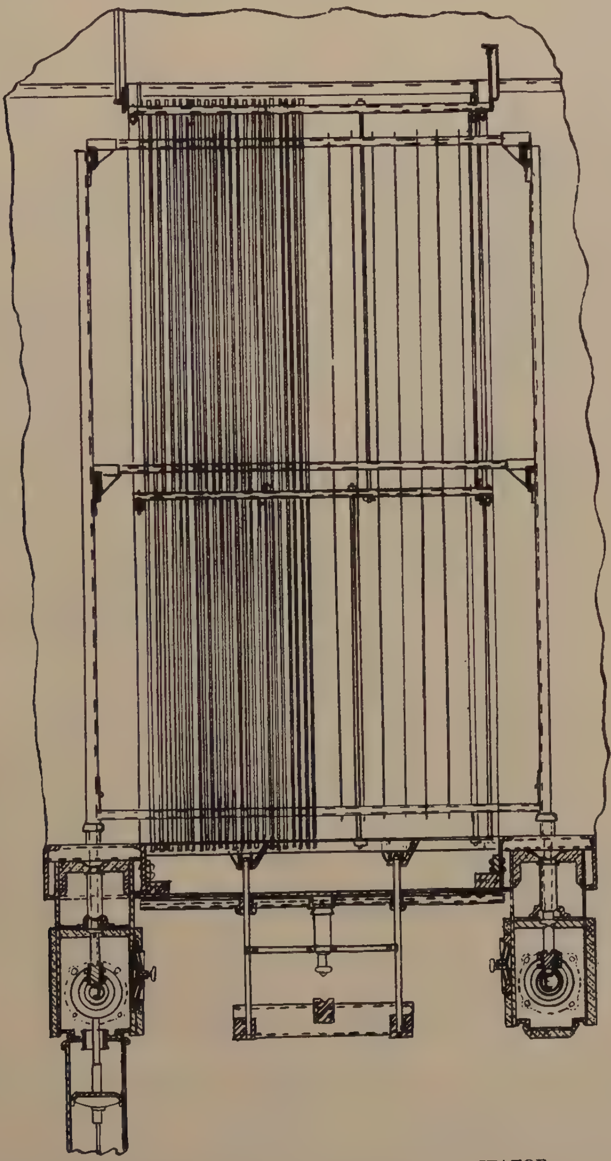


FIG. 5.—ROD-CURTAIN TYPE OF PRECIPITATOR.

tors, such, for example, as the permissible gas velocity through or past electrodes.

Owing to occasional difficulties from buckling or warping of plates, especially in the larger sizes, 12 to 18 ft. high, in a newer type of precipitator plates are replaced by a series of rods on small spacing. Such a precipitator is called the rod-curtain type (Fig. 5), and has proved very satisfactory.

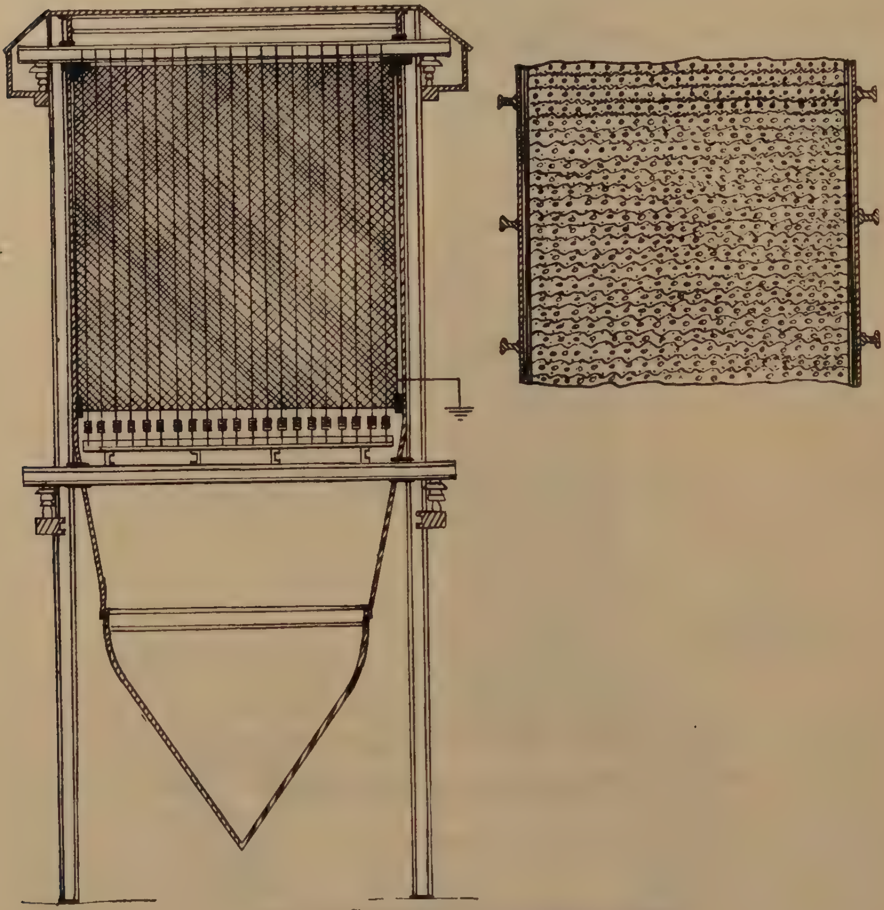


FIG. 6.—SCREEN TYPE OF PRECIPITATOR.

Early work of Cottrell on purification of gases developed a type of transverse screen electrode (Fig. 6) through which the gases passed. This was later developed by Rathbun[28] for lead-smelter work and a number of plants were built. According to Labbe[6], it requires somewhat high relative humidity of the gases for equal conditioning.

A type reported in the patent literature[29], and mentioned by Labbe[6] as in service in Mexico, provides for a cylindrical-rod cylinder (Fig. 7) with central discharge wires and transverse passage of the gases. It would be expected to show a higher efficiency than the screen or wire type.

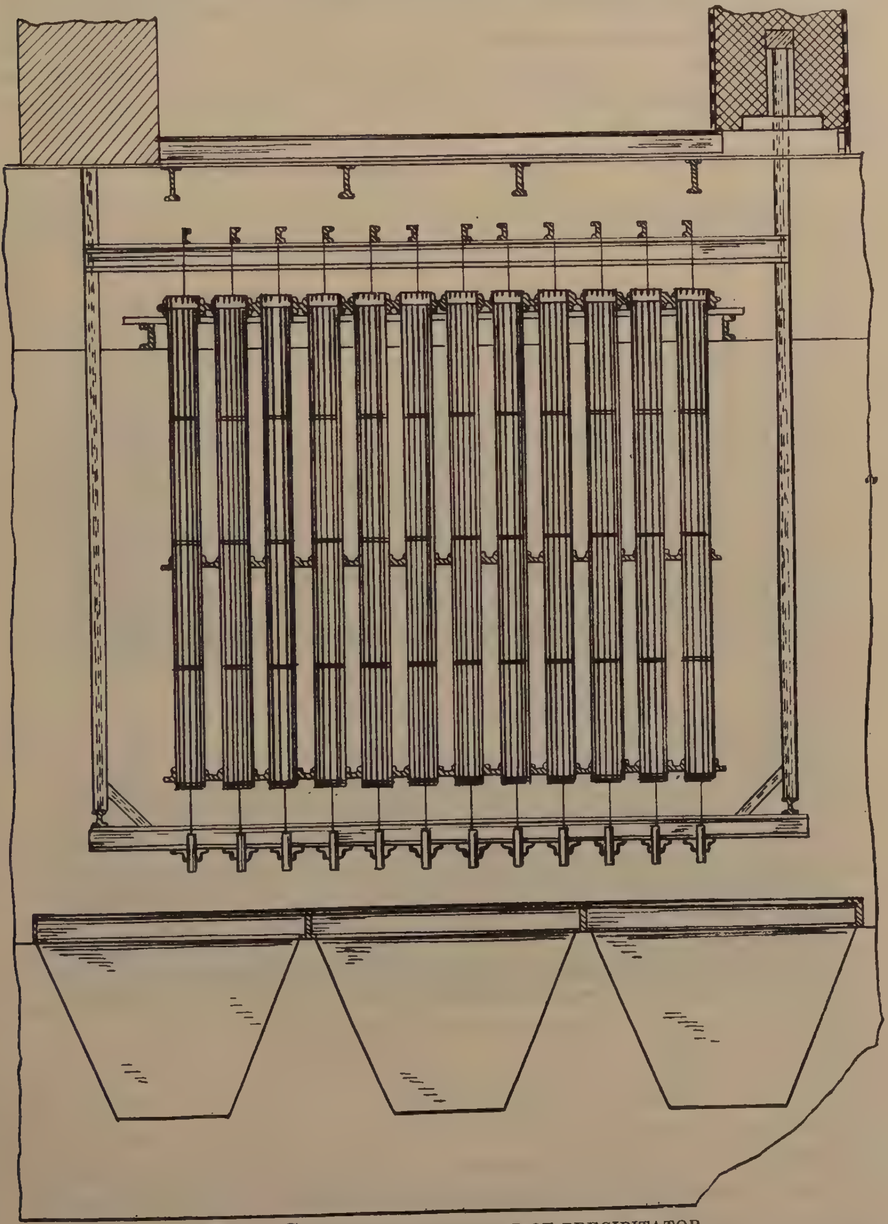


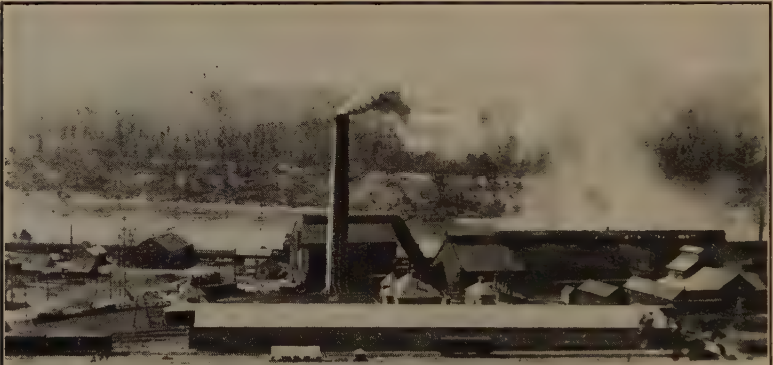
FIG. 7.—CYLINDRICAL-ROD TYPE OF PRECIPITATOR.

PLANT DESCRIPTIONS

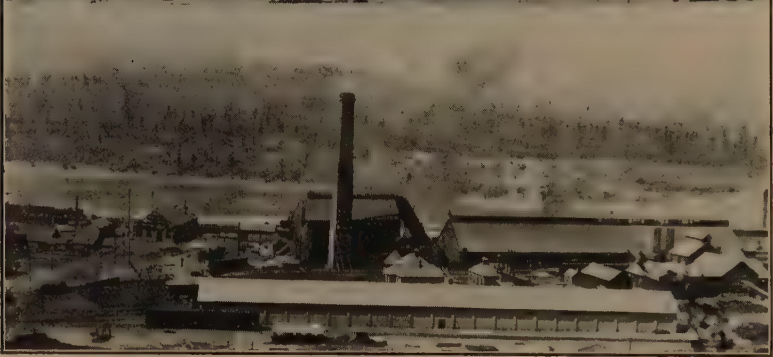
Rulings within certain companies make it impossible to describe their dust and fume-collection plants, but full freedom has been granted by some companies and limited freedom by others, so that a fair cross section of modern plant operation is offered.

Northport Smelter

Although the Northport smelter of the Northport Smelting & Refining Co., Northport, Wash., was dismantled in 1922, the precipitator is still in service at a magnesite-calcining plant. This plant represents an early type not now extensively used in this country because of cost but still widely used in Europe. The plant was built during war days of 1917 and went into operation in January 1918. At the time of its construction conditioning of gases was little understood and this plant went through the full development from unsatisfactory operation without sprays to complete and satisfactory operation with the full complement of sprays to provide necessary cooling and humidification. (Figs. 8 and 9)



8



9

FIGS. 8 AND 9.—NORTHPORT SMELTING & REFINING CO. PLANT.
Fig. 8. Precipitator with power off. Fig. 9. Precipitator with power on.

The plant, using copper-plant experience and assuming (on most restricted observation) on the order of twice the electrode requirements in lead-smelter gases over that of copper roasters, was planned on a basis of 200,000 cu. ft. per min. of copper-roaster gases and in actual operation and with fully conditioned gases handled slightly over 100,000 cu. ft. per min. at approximately 96 per cent collection efficiency. This relative capacity in gas volume between copper roasters and conditioned lead-smelter fumes is substantiated by experience from other plants.

Plant design called for 14 Cottrell units, each unit comprising a tube section of 64 pipes 12 in. in diameter by 16 ft. long, with inlet and outlet damper and flue connections to main inlet and outlet flues. On gases all units were in parallel operation. Seven 15-kva. motor-generator electrical sets were provided, each supplying power to a 15-kva. 220 to 100,000-volt special Westinghouse Cottrell transformer. Two Cottrell units were connected in parallel to one electrical set. Of the 14 units proposed in the design, only 13 were constructed and placed in operation. The design was that of an exposed-pipe type, downdraft, and a large brick flue some 500 ft. long connected the furnaces to the Cottrell and stack. Originally no provision was made for gas conditioning, and after the plant started up, marked effects of back ionization and poor conductivity of deposit developed. Efficiency was around 70 per cent with peak voltage on electrodes, 55 kv. peak and primary reading on switchboard of 45 amp. and 180 volts. Sprays delivering around ½ gal. per min. were installed in groups of six, and during test periods the steam from a 120-hp. boiler was added, which, with 42 sprays in service, resulted in thorough conditioning. Voltage that could be maintained across the electrodes rose from 55-kv. peak to 85-kv. peak; primary amperes on the individual electric machines dropped from 45 to 30 amp.; voltage rose from 180 to 200 and 210 volts. Later tests showed an effect from 60 water sprays equal to that secured from 42 sprays plus steam output of the 120-hp. boiler. Eventually 84 sprays in the flue were made available with normal operation on about one-half this number, night operation requiring on the average a dozen fewer sprays than day operation. Precipitator outlet temperature commonly approximated 150° F. and a relative humidity of around 40 per cent. However, improved operation was noted at 100° to 115° F. and 60 to 70 per cent relative humidity.

Because the flue was used as a spray chamber and relatively low-pressure water sprays were employed, there was an appreciable amount of water particle suspension carried into the precipitator, and as this type of exposed-pipe precipitator allows more chilling of outer rows of tubes, in less than a year a definite corrosion problem appeared. This was corrected, in the main, by housing-in the units, and by a careful control of the number of sprays in operation, always keeping these at the minimum of good operation.

Collection commonly averaged somewhat under 20 tons per day, of about 75 per cent lead and 3 to 4 per cent zinc.

Bunker Hill Smelter

The precipitator at this plant, in its present form, has most successfully overcome such difficulties as developed at the Northport plant. The smelter and the Cottrell plant have been excellently described by Beasley, Feddersen, Schuettenhelm and Johnson[30]. The precipitator is of the submerged-pipe type, consisting of 14 units in two parallel rows, downdraft with 64 pipes per unit, each pipe 12 in. in diameter by 16 ft. long. The discharge electrode is No. 18 wire held straight and taut by a bottom weight. The gases pass down through the tubes and up around the tubes on their way out, so no chilling and corrosion result. The housing for each unit and of the entire installation is of brick, and uniformity of temperature and humidity is constant throughout. The Cottrell receives the gases from the Dwight-Lloyd sintering machines, a maximum volume of 120,000 cu. ft. per min. At the entrance to the spray chamber, the gas temperature is 200° to 250° F.; at the entrance to the Cottrell plant 100° to 125° F. Relative humidity as measured in the Cottrell outlet flue is 50 to 60 per cent.

The sprays operate under 250-lb. pressure and deliver from 25 to 50 gal. of water per minute, the minimum during winter conditions, the maximum in the summer season.

Required electrical energy for Cottrell units is supplied by four motor-generator-rectifier sets, three of which are 15 kva. and one 30 kva. Cottrell transformers are 200 to 100,000 volts. Commonly but three out of the four power sets are in service and the high-tension switching system permits any three of the four sets to serve the three feeder lines of the precipitator, and any unit may be connected with one of two feeder circuits. Unique at this plant is the placing within the gas chamber the porcelain insulators supporting the high-tension electrode, an alteration that has proved most satisfactory, owing to the consistent and skillful plant operation. A further innovation is an automatic timer and reset on the circuit breaker of each electrical unit so that a flashover or arc within the precipitator sufficient to open the circuit breaker will permit the closing of the circuit breaker automatically on 15-sec. intervals three successive times before the operator needs to give it his attention. With the facilities afforded by such devices as this plus the over-all good engineering design and excellent construction, this plant operates with one attendant on duty.

The Cottrell collected dust is accumulated in brick chambers under the precipitator units and after sintering is removed by hand. The collection amounts to approximately 150 tons per month with the following analysis: Ag, 7.5 per cent; Cu, 0.05; Pb, 67.0; Fe, 0.8; insol., 1.0; CaO, 0.2; S, 1.0; Sb, 0.6; As, 0.6.

Sullivan Mining Company

The electrolytic zinc plant of the Sullivan Mining Co. is about one mile from the Bunker Hill smelter and has been very completely described by Messrs. Woolf and Miller[31] and also in this volume, page 527.

The roasting of the zinc flotation concentrates is accomplished in five 25-ft. eight-hearth Wedge roasters each with a normal rating of 40 tons feed per day. Furnace gases are discharged to a steel flue, which extends to the Cottrell plant and stack some 1150 ft. to a hilltop and 232 ft. above the roaster plant. The Cottrell is directly at the base of the stack. No fume is present in the gases, the suspended material being simply zinc flotation concentrates, a mixture of raw, partly roasted and completely roasted fines. Because of the sulphide roasting, the gases are acid in character and no conditioning is required. The precipitator consists of two plate units and is arranged for five plates in series, of which the first, second, third and fourth plates are installed. Each section is a unit comprising 17 plates in parallel providing 16 ducts or gas passageways. Plates are built of corrugated iron sheets 10 ft. high, 9 ft. long (in the direction of the gas flow) and are spaced on 8-in. centers. Discharge electrodes are of wire with weights attached. Two electrical power sets with synchronous-motor rectifiers and 15-kva. 400 to 60,000-volt single-phase transformers energize the electrode system. Efficiency of recovery is very high and the plant from the starting of operations has been fully satisfactory.

Trail Smelter

The plant of The Consolidated Mining and Smelting Company of Canada, Ltd., at Trail is extensive and carries forward a number of metallurgical and chemical processes. These have received much publicity and the reader is referred to the series of four articles by George F. Young[32], for very complete works description; also to pages 59, 271, 540 and 721 of this volume. The management has been forward-looking and was the first to install a large Cottrell plant on lead smelter fumes, in 1914. It was of the exposed-pipe type, originally of 12 sections, each section of 32 pipes; pipes were 13-in. O.D. standard well casing, ¼-in. wall and 15 ft. long. It has been enlarged to 18 sections and in 1925 was largely reconstructed. The Cottrell exposed-pipe precipitator has been operated under several technical procedures. Originally an updraft design, it has, from time to time and for periods of test operation, been operated with some units downdraft and again with units in series and in parallel service. The present operation is as an updraft precipitator with all sections in parallel, and it is modified to the extent of a wooden housing as weather protection for each unit.

At the time of its original construction in 1914, the necessity of conditioning of gas and suspended fume content was unknown and a great deal of experimental investigation was carried on by the technical department of the smelter. Parallel with work at other plants, particularly Northport, Trail investigators developed the spray system and spray chamber.

The blast-furnace gases are now conditioned in a large spray chamber equipped with 300 sprays, each with a delivery capacity under 275-lb. water pressure of approximately ¾ gal. per min. Variation of number of sprays in operation is from approximately 100 during the winter season to 300 during the summer. The construction and operation of the spray chambers are special to this plant. All the sprays are concentrated in the inlet end of the chamber, the remainder of the chamber thus forming a settling area for the dropping of the coarse, suspended water particles. All sprays discharge horizontally and in the direction of the flow of the gases. Approximately 20 per cent of the spray water is evaporated into the gases, and control provides for a minimum of 4 to 5 per cent of moisture in the precipitated dust.

Operating in parallel with this pipe Cottrell is a second precipitator of the plate type. Its installation is due to more extended smelter-plant operations and the selection of plates over pipe was due to the compactness of this design, its lower first cost per unit capacity and the fact that conditions for corrosion are much less pronounced in this plate design than in the exposed type.

In the several steel-plate precipitators installed at this reduction works, the same general unit design of electrodes has been followed, the plants then varying in the number of Cottrell units in parallel, the number of electrodes in parallel in each section and the number of electrodes in series in each precipitator unit. The unit design of electrode provides for plates 10 by 10 ft. with vertical, large corrugations, the latter on 5½-in. centers. In a duct or electrode-gas passageway, two such plates are mounted with the convex and concave corrugations directly opposite each other, the discharge electrode (a vertical wire) being placed central to each pair of concave corrugations. There is thus a discharge wire to each 5½ in. of horizontal length of plate. As there is a cross member support for the top bus bars on the middle line, which requires the omission of one or two discharge wires at this point, there are actually 20 discharge wires to a 10-ft. length of plate (in the direction of gas flow). This approximates the idea of a continuous series of 20 pipes, incomplete as to full circumference, with passage of the gas along the longitudinal length of tube and past 20 electrodes in series. It is, therefore, a special form of horizontal gas-flow plate precipitator. Plates are of ⅛-in. "Key-stone" stock, factory-corrugated, and have given good satisfaction in service.

This plate Cottrell operating in parallel with the pipe precipitator consists of four units each with its own inlet and outlet dampers and electrical power set. The four units are in parallel operation. Each unit has four sections in series and each section contains 13 plates, 12 ducts or gas passageways, with a 12-in. spacing center to center of plates. Discharge electrodes are of No. 9 B. & S. wire held tensioned by weights.

A substation contains the electrical sets for both the pipe and plate precipitators. This comprises 10 electrical power sets, each set composed of a 40-hp. induction motor direct-connected to a 25-kva. single-phase generator and through a shaft extension to the rectifier. The circuit from each single-phase generator passes to a high-potential transformer of 220 to 60,000 volts and for each electrical set there is suitable control board with indicating voltmeter and ammeter. By transformer ratio the power sets connected to pipe units provide a voltage to precipitators of 60,000 volts; to plate units of 65,000 volts. Current flow per electrical machine to Cottrells approximates 165 milliamperes to plate units and 250 milliamperes to pipe units. Four electrical sets are connected to four pipe sections each, two electrical sets to six pipe sections each and four machines, one to each Cottrell unit, to the plate precipitator.

Rapping on both units is done by hand, discharge electrodes on 1-hr. intervals and collecting electrodes on 2-hr. intervals.

Cottrell Precipitator on Gases from Dwight-Lloyd Sintering Machines

At the Trail plant there are 14 Dwight-Lloyd sintering machines producing 1400 tons of sinter per day. The recovery of the solids discharged with sintering-plant gases has at all lead works been a problem more of maintenance of equipment than of process. The gases carry considerable acidity, while the suspended solids are largely true fumes. The reducing action on the moving grate often brings into the gases elements of high combustibility such as elemental lead, arsenic, antimony and sulphur. The latter is a particularly troublesome element, igniting spontaneously if allowed to collect and dry out in dead pockets and requiring more thorough humidification for satisfactory collection than the other elements present. During recent years the improvement in flotation practice by which the major portion of the pyrites is removed from the lead and zinc concentrates has greatly lessened the problem of free sulphur in Dwight-Lloyd gases, and while a minor or scarcely considered problem at Trail, it is still at other plants a lively consideration in plant work.

The corrosion problem in the Cottrell is that due to precipitated, suspended spray-water droplets and condensed vapor from the cooling of saturated gas and resultant wetting of deposit and interior structural parts. It becomes more of a problem solely because of uncontrollable irregularities of sintering-plant operation, which vary the minimum requirements for spray water over a wide range. While operation characteristics of rectifier and switchboard readings indicate precisely either an insufficiency or sufficiency of water-spray conditioning, they give no evidence of excessive spray operation and only close visual inspection at inlet flue and precipitator plus judgment and experience will permit spray control to minimum requirements. In practice it usually cannot be quite obtained and at Trail this corrosion problem has been overcome by replacement of the steel collecting plates by similar plates of pure aluminum metal.

The Cottrell at the Dwight-Lloyd plant consists of seven units in parallel, each with its own inlet and outlet dampers. Each unit consists of four sections in series and each section of 19 plates or 18 ducts or gas passageways. Each plate is 10 by 10 ft. of 3⁄16-in. aluminum plate corrugated on 5½-in. centers. Spacing center to center of plates in 8 in. Discharge electrodes are of No. 9 hard-drawn iron wire, tensioned with weights. While aluminum wires and small rods have been utilized as discharge electrodes and have resisted corrosion excellently, the sparking continually in evidence where they passed through the lower grid guide gradually reduced their section until rupture occurred and the iron wires have proved the most satisfactory.

Power for this Dwight-Lloyd precipitator is provided by seven electrical sets installed in a special substation building. Each set supplies one unit of the precipitator. This substation plant differs from the plant described earlier in the paper, in utilizing synchronous motor-driven rectifiers with current supply from the 550-volt 60-cycle power lines. Each of the seven sets is provided with a 25-kva. 550-volt primary 25,000 to 60,000 secondary transformer, with winding taps brought out on 5000-volt steps from 25,000 to 60,000 volts. Switchboards per set provide the usual primary volt and ammeters, multiple-point switches both for transformer tap and rheostat resistance control, reversing switch for transformer leads and motor controls. The current to precipitator per machine approximates 300 ma. and voltage by transformer ratio 50,000 volts.

A large spray and water-droplet settling chamber is provided for Dwight-Lloyd gases, operating in all respects as the spray chamber for blast-furnace gases. As many as 400 sprays at 275-lb. pressure are used in the summer season. Multistage centrifugal pumps have given the most satisfactory operation for this service. For Dwight-Lloyd gases two pump units are provided, each unit comprising a 100-hp. motor direct connected to a six-stage Allis Chalmers centrifugal pump capable of delivering 200 gal. of water per min. against a 275-lb. head.

Precipitators on Zinc Sulphide Furnaces at Trail

Trail is quite as important in the world's zinc-production activity as in the lead-producing field and some 700 tons of zinc flotation concentrates are furnaced daily. Gas cleaning can be done in either of two precipitation plants. The older precipitation plant was originally installed to treat the gases from 21 Wedge roasters. At present two of the three units can if necessary receive the gases from any of the eight furnaces burning the zinc sulphide concentrates while in suspension (so-called flash roasting) and the third unit cleans the gases from the reverberatory furnace melting zinc cathodes. No conditioning of the gases is required and the collection is largely dust with some fume. As is usual in sulphide roasting, the gases provide sufficient acidity to be readily conductive.

Each unit of this three-unit plant is complete with its own inlet and outlet dampers and electrical connections. Each unit contains six sections in series, of which four sections are equipped with electrodes. Each section contains 16 collecting plates and 15 ducts or gas passageways. Collecting plates are of corrugated steel sheets ⅛ in. thick and 10 ft. long by 12 ft. high. Corrugations are on 5½-in. centers and vertical and the spacing center to center of plates is 12 in. Discharge electrodes are No. 9 hard-drawn iron wires, 24 to a section duct. Construction is of steel and walls of double gunite on steel reinforcement.

Three motor-generator sets identical with those in service at the blast-furnace Cottrell plant serve this precipitator, one to each Cottrell unit. The precipitator charging current approximates 110 ma. per machine and by transformer ratio 62,000 volts.

The newer plant treating the gases from zinc sulphide burning is direct-connected with the large-scale acid-manufacturing plant. Eight furnaces burn 700 tons of zinc sulphide concentrates per day.

There are eight units in the Cottrell precipitator; all units are two sections long. Two units have sections of 11 plates and 10 ducts, and six units have sections of 15 plates and 14 ducts. Collecting plates are 12 in. center to center, or spacing. Plates are of the corrugated type standard at this smelter; 10 by 10-ft., ⅛-in. thick plate with vertical corrugations on 5½-in. centers. There are 24 discharge electrodes per section duct of No. 9 hard-drawn iron wire. Framing and supports are of structural steel with the housing of 13-in. brick wall.

Four power units with synchronous-motor rectifier and 25-kva. transformers, similar to those installed in the Dwight-Lloyd plant, supply the power to the treater units, one power set to each two units. Electrical energy to Cottrells and from each power set average 160 ma. at voltage by transformer ratio of 45,000 volts.

Reverberatory Furnace Refining Slimes from Electrolytic Lead Refinery

At the Trail smelter a Betts process plant for the refining of lead by the electrolytic process is in operation with a capacity of 450 tons of refined lead per day. The handling and refining of the slimes from this electrolytic operation is accomplished in a reverberatory furnace. The furnace gases carry a true fume of lead products, and plant operation and practice follow closely the operations at the blast-furnace plant.

The precipitator consists of two units in parallel, each unit of five sections and each section of six plates, five ducts or gas passageways. Plates are of the standard described, 10 by 10 ft. and 5½-in. vertical corrugations, spacing between plates 12 in. Discharge wires, 24 to a section duct and of No. 9 hard-drawn iron. The structural parts are of steel with housing of double gunite walls. Spray-chamber operation is similar to that of the blast-furnace gases. Power equipment of two units of motor-generator sets is identical with the equipment on the blast-furnace Cottrell plant. Power input to precipitators per electrical set is approximately 75 ma. at 60,000 volts by transformer ratio.

Acid-plant Mist Precipitator

It was mentioned that part of the treatment plant provided under zinc-roaster gases served the new acid plant. In addition to the dry cleaning of the gases by Cottrell precipitators, there is a further installation of Cottrell units as mist collectors in the purification of the gases preceding their entrance to the contact plant. This new acid plant has been fully described by W. M. Cobleigh[33]. The installation of mist precipitators for gas purification consists of 18 units in parallel service. Each unit is of lead construction within a cylindrical steel shell with independent inlet and outlet jug dampers. Each unit contains 21 lead pipes 10 ft. long and 6 in. in diameter. It is of the submerged type, the gas passing down around the tubes and up through them. Discharge electrodes are of star-shaped lead-covered iron wire supported through a central electrode, which is carried outside the precipitator shell through an oil-seal bushing. About 50,000 volts is maintained between electrodes, the power set being of the standard design for this plant.

Mount Isa Smelter

The development of Mount Isa Mines, Ltd., Mount Isa, Queensland, Australia, marks the latest discovery and most recent large-scale construction of a new and sufficiently important producer in lead and zinc to be a prime consideration in the world's markets. The mine, mill and smelter have been described by J. M. Callow[34].

Blast-furnace and Dwight-Lloyd gases are mixed, passed through a spray chamber, a settling flue, the Cottrell plant and to stack. Present operations require seven out of eight Dwight-Lloyd machines and one out of three blast furnaces in service. The charge to the sintering machines is 1400 tons a day, to blast furnace 300 tons, with average lead production of 100 tons per day. The Cottrell installed with the original smelter, a two-unit plant, received the gases from three Dwight-Lloyd machines and one blast furnace. Gas volume was approximately 90,000 cu. ft. per min. and efficiency of collection 95 per cent. With the installation of additional Dwight-Lloyd machines, a third unit was added.

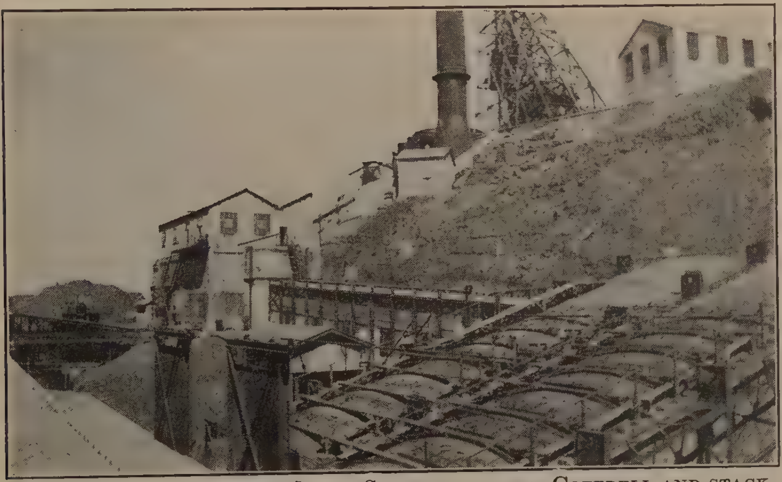


FIG. 10.—MT. ISA MINES, LTD. SPRAY CHAMBERS, COTTRELL AND STACK.

The precipitator is of the so-called rod-curtain type, ⅛-in. standard pipe being used, on 2-in. centers. These curtains are 12 ft. high by 7 ft. 4 in. long (in the direction of gas flow). Each of the three units installed is complete with its own inlet and outlet multivane dampers. Each unit comprises four sections in series and each section carries 16 rod curtains, 15 ducts or gas passageways. Spacing between plates center to center is 8 in. Discharge electrodes are ⅛-in. square, twisted rods, spaced on 8-in. centers, held in position by a steel framework and supported on insulators mounted in overhead insulator compartments. The curtains are rapped by hand-operated air hammers acting on anvils mounted on each rod-curtain frame and carried through the top covers. High-tension discharge rods are rapped through a system of hammers within the precipitator, striking on frame members and operated by a hand lever from the operating floor of the precipitator.

The substation is directly above the inlet header with its floor level with that of the operating floor of the main precipitator, an arrangement of much convenience to the plant operator.

The three-unit plant has seven Cottrell power sets. Each set comprises a synchronous-motor-driven rectifier, 15-kva. high-potential transformer, 440 volts primary and 40,000 to 60,000 volts by 5000-volt taps secondary. Each set has its own control and instrument board. Six power sets are in continuous service, one to each two sections of precipitator, with one set as a spare.

Precipitated dust is collected in longitudinal hoppers, one to each unit, removed by ribbon screw conveyors pugged with water, and with the spray-chamber discharge is recovered from a Dorr thickener as a thickened pulp and joins the mill concentrate to Dorrco filters.

Two spray chambers in parallel, each 20 ft. wide, 20 ft. high and 72 ft. long, have a spray system providing a total of 224 sprays, each capable of delivering 0.4 to 0.5 gal. of water per min. under 250 to 300 lb. pressure. The number in operation varies widely with weather conditions. The spray system is served by two pump units, one in service and one as spare. Each pump unit comprises a six-stage centrifugal pump direct-connected to 45-hp., 2920-r.p.m. electric motor. Temperature at the entrance to the spray chamber varies from 250° to 300° F., at the outlet of the Cottrell about 115° F., with the collected dust averaging about 4.6 per cent moisture.

Electrolytic Zinc Company of Australasia, Ltd.

This company operates an extensive electrolytic zinc plant in Tasmania and in connection with its requirements for roasting of Broken Hill zinc sulphide concentrates operates several acid and phosphate fertilizer plants in Tasmania and on the mainland of Australia. In connection with two of its related activities it operates Cottrell units as mist extractors where scrubbers had failed to give the efficiency desired.

The electrolytic zinc plant at Risdon, Tasmania (Fig. 13), has been fully described in several papers[35,36,37] and in this volume (p. 482).

First or primary roasting of the zinc sulphide concentrates is accomplished at acid plants on the mainland, and the calcine, then averaging approximately 7 per cent sulphur, is given its second and final roast at the Risdon plant. This second roast is accomplished in a coal-fired modified Leggo furnace of four superimposed hearths. Gases from these furnaces pass to cyclones, thence to sea-water scrubbing towers for removal of suspended dust and SO_2 gas and thence to a lead-pipe precipitator of five units for removal of sulphuric acid mist, then exit through a wooden stack to atmosphere. The problem was not the recovery of the acid mist for its value but to remove the mist from the atmosphere as a measure of efficient plant operation and the avoidance of a nuisance. Good operation is indicated by a nonvisible stack discharge. The five units are arranged in parallel, are supported in a steel framework, with all surfaces in contact with the gases made of sheet lead. There are 50 lead pipes

12 ft. long to a unit. Construction is of the exposed-pipe type, the gas passing upward through the tubes. Discharge electrodes are of star-shaped lead-covered iron wires, held in tension by weights.

Power for the five Cottrell units is provided by five synchronous-motor rectifiers connected to five 220 to 75,000-volt special Cottrell transformers. The usual form of switchboard and tap resistance control is provided. Operating voltage varies from 65,000 to 85,000. Cleaning of the tube units is effected by flushing with salt water, and commonly on 4-hr. intervals. The plant has always functioned satisfactorily.

At the Port Pirie lead smelter of Broken Hill Associated Smelters, the Electrolytic Zinc Co. has in operation a contact acid plant and provides for this plant's SO_2 requirements through the primary roasting of Broken Hill concentrates. These concentrates contain appreciable quantities of many minor elements, among the most objectionable from the point of view of acid making being chloride, fluorine and arsenic. An extensive gas-cleaning and purification system precedes the contact chambers, and incorporated therewith as a means of removing the final traces of arsenic, lead sulphate and acid fume is an electrical precipitator consisting of eight units in parallel, all of lead construction and each inside a steel housing. Each unit has its own inlet and outlet jug dampers and carries 21 lead pipes 6 in. in diameter by 10 ft. long. Gas passes down around the pipes and upward through the tubes. It is thus a submerged-pipe type of precipitator. High-potential discharge electrodes are star-shaped, lead-covered iron wires and are supported overhead through a central spider frame and tensioned by weights at their lower ends. The overhead support for the discharge electrodes is carried outside the unit through an oil-seal bushing to porcelain supports. In

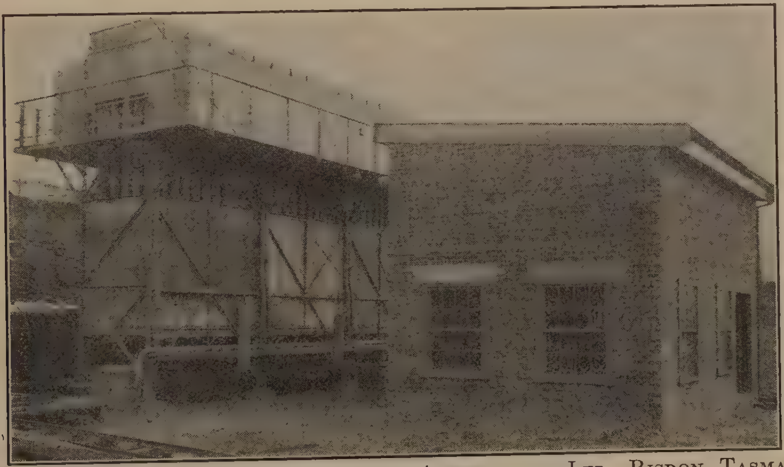


FIG. 11.—ELECTROLYTIC ZINC COMPANY OF AUSTRALASIA, LTD., RISDON, TASMANIA. Cottrell on gases from Leggo furnaces.

order to protect this oil seal from the moisture-laden gases, a small return of dry gas taken past the drying towers is returned and discharged at the oil-seal surface line. Collection by the Cottrell amounts to a "drip" of 1600 gal. per day carrying 1.3 lb. As, 4.0 lb. Cl and 560 lb. H_2SO_4 plus a considerable quantity of $PbSO_4$. Two 12-kva. motor-generator-rectifier sets are provided, each connected to a transformer of 355 volts primary and 66,000 secondary. (Fig. 12.)

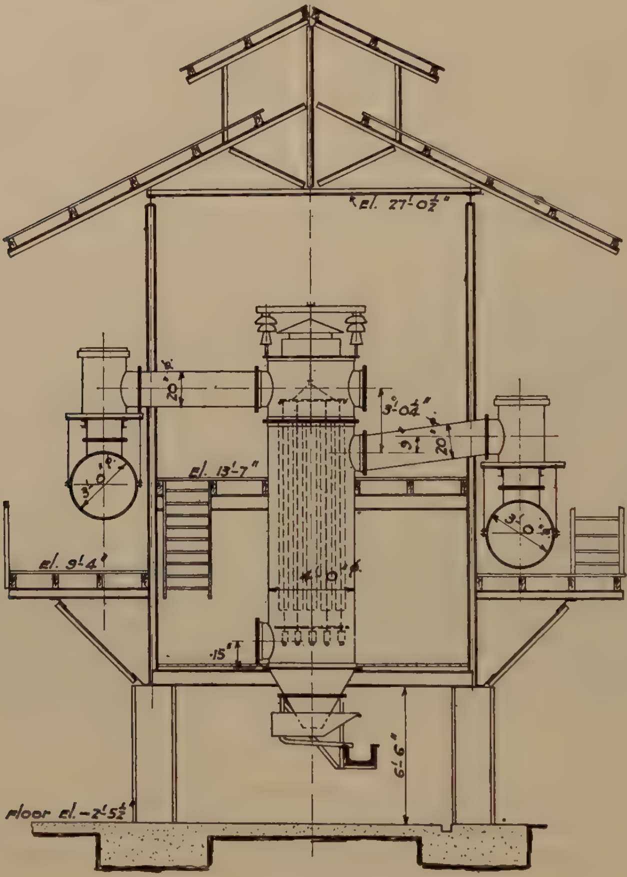


FIG. 12.—ELECTROLYTIC ZINC CO., PORT PIRIE, AUSTRALIA.
Lodge-Cottrell mist precipitator for purification of gases to contact acid plant.

American Smelting and Refining Company

The American Smelting and Refining Co. operates a number of lead smelters in this country and in Mexico. In some of its copper-smelting operations it has collection plants for the basic fume from the lead and zinc present in copper-plant feed. Little information as to their plants has been published, Labbe's paper[6] providing the following notes.

The Murray plant has a pipe precipitator taking gases from Dwight-Lloyd machines and Wedge roasters. This combination of gases provides a precipitate of good conductivity. The East Helena plant has a pipe precipitator handling gases from Dwight-Lloyd machines. It is conditioned by water sprays to 45 to 50 per cent relative humidity.

At the Rosita zinc smelter, Coahuila, Mexico[38], gases from four 20-ft. dia. Skinner furnaces are treated in a four-unit, three-section plate-type Cottrell.

Eastern United States

While the middle and western states are mainly producers of primary metals, the eastern states do the major portion of the refining and secondary metal recovery. Primary production is in relatively few large plants, well equipped and therefore simple of description. The great number and variety of operations and the general small volume of individual secondary plants make description of individual plants out of the question and, therefore, only general description will be offered here.

The secondary recovery of metals is an expanding activity and while for some time the plants built were often crude and inadequate, the newer plants are generally provided with suitable baghouses or Cottrell precipitators. Owing to the relatively small gas volume and easier conditions for gas conditioning which the exposed pipe offers, many units of this type have been installed. They vary in size from ten to a dozen pipes up to fifty and from one to several units. Synchronous-motor-rectifier sets are commonly supplied with 5 to 15-kva. transformers with operating voltages of 30,000 to 60,000 volts.

A typical example is the following plant: Gases from a blast furnace handling 50 tons per day of battery plates, slags and drosses. Gas volume is 3700 cu. ft. per min. at 220° F. Precipitator is one unit of exposed pipe, 24 tubes; fine wire discharge electrodes, water added to charge for gas conditioning; efficiency of collection 96 per cent. Power unit has one synchronous-motor-driven rectifier, one 210 to 75,000-volt transformer, one switch and control board.

A second similar plant of equal tonnage capacity and gas volume has a two-unit plate precipitator. Each unit is one section long of nine ducts, with plates 3 ft. high by 6 ft. 6 in. long. Additional conditioning to wetting down of charge to furnace is one steam and one water spray in flue ahead of precipitator. The efficiency is 90 per cent, and the power set the same as in the previous example.

A third example is a converter operating on secondary metals, scrap brass and some matte. Gas volume is 18,600 cu. ft. per min. at 150° to 160° F., conditioned by 39 Schuette & Koerting sprays delivering approximately 22 gal. of water per minute, of which 45 per cent is retained in gases and precipitate. With intermittent operation, approximately 95 per cent collection; 4 tons per day. Precipitator of two units, each one section long, 19 plates, 18 ducts. Collecting plates 8 ft. high by 6 ft. long, 6-in. spacing center to center of plates. Discharge wires No. 9 iron wire. Power equipment, one 15-kva. transformer, primary voltage 200 secondary 55,000 to 75,000 by 5000-volt taps. Synchronous-motor rectifier and usual instrument and control board.

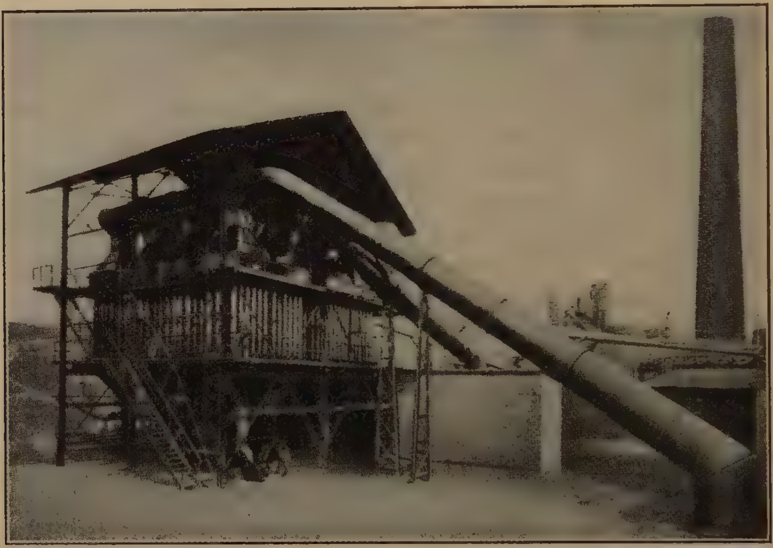


FIG. 13.—PLANT IN SAXONY, GERMANY. (*Lurgi Apparatebau Gesellschaft.*) Precipitator cleaning refinery and lead blast-furnace gases.

A further application, entirely outside the field of secondary metal recovery, is the use of precipitators on hot gases from zinc roasters supplying chamber-acid plants. It is essential in this service that the gases be cleaned at the prevailing temperature provided by the furnacing of zinc sulphide concentrate, which is 1000° to 1100° F. The gas volume at that temperature is 30,000 cu. ft. per min. The precipitator has two units, each of two sections, each section of 13 plates, 12 ducts or gas passageways, 8-in. spacing center to center of plates. Wire discharge electrodes are used, all metal parts are of high-chrome alloy and walls of steel lined with insulating and firebrick. Automatic rapping of discharge and collecting electrodes is provided. Collection is 5 to 6 tons per day at 95 to 97 per cent efficiency. One electrical set with operating voltage across electrodes approximately 65,000 volts. An exposed-pipe precipitator at a German refinery and lead blast-furnace plant is shown in Fig. 13.

Waelz Process Plants

The Waelz process has found extensive application in zinc and lead metallurgy in Europe, more particularly in Germany, but only to a very limited extent in this country. It has been frequently mentioned in the technical press[40,41] and described with considerable detail by R. Hoffman[39] and in this volume, page 702. While baghouses have been used as collectors for the evolved fumes from Waelz process kilns (Fig. 14), electrical precipitators, or electrofilters, as our German friends designate them, have been far more widely used. Dr. F. Blass has more particularly described electrofilters in connection with rotary-kiln operations[41].

In general the gases from the Waelz kiln are cooled either by passage through a waste-heat boiler or by a tubular air cooler and then passed in series through two or more exposed-pipe precipitator units or a combination exposed-pipe followed by a plate precipitator. Since in this kind of metallurgical plant the fume collection is the full amount of values recoverable from the furnace charge, very high efficiency of collection is essential and the plants are usually designed on a basis of 99 to 99.8 per cent efficiency of collection.

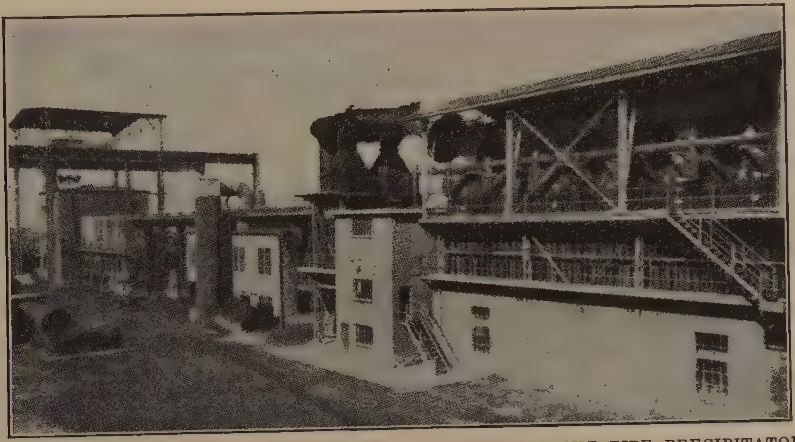


FIG. 14.—EUROPEAN WAELZ PROCESS PLANT WITH SIX-UNIT PIPE PRECIPITATOR IN FOREGROUND. (*Lurgi Apparatebau Gesellschaft.*)

Two American installations are reported by B. H. Strom. Two paragraphs of his article provide information on plant capacity, operation and fume-collecting means and are of sufficient interest to be repeated here:

> The United States Steel Corporation has installed a (Waelz) kiln in its plant at Donora, Pa., for the treatment of muffle residue, current production, and residue from an old dump containing about one million tons. This residue, which already contains enough coal for reduction, is fed directly to a kiln 120 ft. long (36 m.), 10 ft. outside diameter (3 m.), with a capacity of 360 tons per 24 hours, which is expected to be increased to 400 tons. Natural gas is used for auxiliary heating. The plant requires

only four men per shift for operation, the entire installation being mechanized as far as possible. Cottrell precipitation is used for collecting the oxide, which contains little lead and is reduced to metallic zinc by the regular retort process. The over-all recovery has averaged over 95% over several months of continuous operation, and the plant has experienced few mechanical difficulties from ring formation or for any other reasons.

The New Jersey Zinc Company has installed a kiln at its Palmerton plant, 140 ft. long (42 m.), and with 10 ft. outside diameter (3 m.), which treats a varied feed, ore, residues, slime, flue dust, and other metallurgical products, using a cheap grade of coal for reduction, such as screenings from coal washing. This installation has been in operation for only a short time, but the results obtained are satisfactory. The oxide is collected in a baghouse and used for the production of lithopone[37].

Gold and Silver Refineries

It is the usual practice in private refineries of precious metals to pass the gases from the various roasters, retorts, doré furnaces, etc., to ample scrubbing systems, and for many years such collection as these effected was considered as satisfactory. As methods of precision improved within their own operations and procedure for accurate measurement of actual exit gases became available, plus the general better understanding of fume characteristics, it became evident that further worth-while recoveries could be secured from Cottrell precipitators. These are of lead-pipe construction and vary widely in number of pipes to a unit and number of units. Pipes usually are from 8 to 12 in. in diameter and 10 to 12 ft. long. Electric power usually is from a Cottrell set capable of delivering 60,000 to 75,000 volts across the electrodes.

In refineries maintained by governments, however, to avoid the inconvenience and general untidiness of scrubber installations, the collection has been accomplished in a steel precipitator and in dry form, it being recognized that under such operation much larger plants in electrode installation are required and therefore more investment cost. The major government refineries of Europe and North America are so equipped[42].

ACKNOWLEDGMENTS

It is a pleasure to express appreciation for the kindly interest and assistance of Mr. R. K. Blois, of Consolidated Mining and Smelting Company of Canada, Ltd. (Trail); Mr. Julius Kruttschnitt, of the Mount Isa Co., Mt. Isa, Queensland, Australia; Mr. Harry Hey, of the Electrolytic Zinc Company of Melbourne, Australia; and Mr. C. W. Hedberg, of the Research Corporation, New York.

BIBLIOGRAPHY

1. H. V. Welch: *Trans.* A.I.M.E. (1934) **106,** 296–323.
2. F. G. Cottrell: Electrical Fume Precipitation. *Trans.* A.I.M.E. (1912) **43,** 512.
3. W. A. Schmidt: Cottrell Process of Electrical Precipitation. *Trans.* Amer. Inst. Chem. Engrs. (1928) **21,** 11.

4 L. Bradley: Electrical Precipitation of Suspended Particles. *Trans.* Amer. Electrochem. Soc. (1912) **22,** 489.

5. E. Anderson: Some Factors and Principles Involved in the Separation and Collection of Dust, Mist and Fume from Gases. *Trans.* Amer. Inst. Chem. Engrs. (1925) **16,** 69.

6. A. L. Labbe: Application of Cottrell Process in Lead and Copper Smelting. A.I.M.E. Pamphlet 1480 (1925).

7. K. Y. Shiga and Ritaro Hirota: Cottrell Electrical Precipitation Process in Japan. *Eng. & Min. Jl.* (1919) **108,** 895.

8. R. B. Rathbun: Electrical Precipitation of Solids from Smelter Gases. *Trans.* Amer. Inst. Elec. Engrs. (1922) **41,** 815.

9. H. V. Welch and L. H. Duschak: Vapor Pressure of Arsenic Trioxide. U. S. Bur. Mines *Tech. Paper* 81 (1915).

10. C. K. Ingold: Vapor Pressure of Lead. *Trans.* Chem. Soc. (London) (1922) **121,** 2419.

11. J. Johnston: Vapor Pressure of Several High-boiling Metals. *Jnl. Ind. & Eng. Chem.* (1917) **9,** 873.

12. R. W. Millar: Vapor Pressure of Metals and a Few Non-metals. *Eng. Chem.* (1925) **17,** 34.

13. R. W. Millar: *Jnl.* Amer. Chem. Soc. (1923) **45,** 2323.

14. A. Eilers: Notes on Bag Filtration Plants. *Trans.* A.I.M.E. (1912) **44,** 708.

15. H. H. Alexander: The Baghouse in Lead Smelting. *Trans.* A.I.M.E. (1914) **49,** 561.

16. L. S. Austin: The New Baghouse at the Midvale Smelter. *Min. & Sci. Pr.* (1916) **112,** 746.

17. J. F. Cregan: Baghouses for Zinc Oxide. *Eng. & Min. Jnl.* (1918) **106,** 126.

18. A. O. Walker: Brit. Patent 11120 (1884); German Patent 32861 (1885); U. S. Patent 342548 (1886).

19. A. O. Walker: A New Application of Electricity. *Engineering* (London) (1885) **39,** 627.

20. W. A. Schmidt: U. S. Patent 1343285 (June 15, 1920).

21. E. R. Wolcott: Effects of Dielectrics on the Sparking Voltage. *Phys. Rev.* (1918) [N.S.] **12,** 284.

22. E. Anderson: Private Communication.

23. F. W. Peek, Jr.: Sphere Gap as Means of Measuring High Voltage. *Trans.* Amer. Inst. Elec. Engrs. (1913) **32,** 812.

24. E. R. Wolcott: An Electrostatic Voltmeter. *Elec. World* (May 13, 1916).

25. A. B. Young: Tooele Flue-type Cottrell Treater. *Trans.* A.I.M.E. (1920) **44,** 764.

26. G. Lewers: U. S. Patent 1429914 (Sept. 19, 1922).

27. R. B. Rathbun: U. S. Patent 1491274 (April 22, 1924).

28. R. B. Rathbun: U. S. Patent 1381660 (June 14, 1921).

29. R. B. Rathbun: U. S. Patent 1763010 (June 10, 1930).

30. A. F. Beasley, P. C. Feddersen, J. B. Schuettenhelm and J. W. Johnson: The Bunker Hill Smelter. *Min. Congress Jnl.* (1931) **17,** 618.

31. W. G. Woolf and R. M. Miller: Electrolytic Zinc Plant of the Sullivan Mining Co. *Min. Congress Jnl.* (1931) **17,** 624.

32. G. J. Young: Lead Smelting and Zinc Fuming at Tadanac, B. C. *Eng. & Min. Jnl.* (1931) **131,** 415.

33. W. M. Cobleigh: Contact Sulfuric Acid Plant. *Ind. & Eng. Chem.* (1932) **24,** 717.

34. J. M. Callow: The Mt. Isa Lead-zinc Plant. *Min. and Met.* (June, 1932) 281; also *Eng. & Min. Jnl.* (1932) **133,** 371.

35. H. C. Urquhart and K. I. Marshall: Electrostatic Precipitation of Suspended Particles from Gases. *Proc.* Australasian Inst. Min. Engrs. (1923) No. 52, 223.

36. Manufacture of Sulfuric Acid. *Chem. Eng. & Min. Rev.* (Melbourne) (Jan. 5, 1928) 120.
37. General Superintendent and Staff, Electrolytic Zinc Co.: Risdon Works of Electrolytic Zinc Co. of Australasia, Ltd. Paper before Australasian Inst. of Min. and Met., August, 1934.
38. W. J. Jenni and R. F. Spooner: Zinc Smelting in Mexico. *Eng. & Min. Jnl.* (1931) **131,** 558.
39. R. Hoffmann: The Waelz Process. *Trans.* A.I.M.E. (1928) **76,** 537.
40. B. H. Strom: The Waelz Process. *Eng. & Min. Jnl.* (1930) **130,** 56.
41. F. Blass: Anlagen für Metallhütten (Electrofilter). *Metallwirtschaft* (1931) **10,** 244.
42 N. W. Sultzer: Recovery of Gold at the U. S. Assay Office, New York. *Chem Age* (January, 1925).

History of the Metallurgy of Zinc

By W. R. Ingalls,* Member A.I.M.E.

In reviewing the history of the metallurgy of zinc, I shall pass hastily over what is only of antiquarian interest. That has been excellently treated by Dr. Bernhard Neumann in "Die Metalle" (1904) and has been described briefly in my "Production and Properties of Zinc" (1902), in my "Lead and Zinc in the United States" (1908), and in other metallurgical works of more or less the same date. In this present monograph, I have it in mind to confine myself mainly to technical practice, especially to that of the last 75 years, prior to which period advance was slow and of no great moment.

The ancients made brass by the cementation process, i.e., embedding copper in a mixture of calamine and carbon and heating, whereby zinc oxide was reduced and zinc was vaporized and combined with the copper. Zinc was isolated by some of the alchemists, who named it and knew something of its properties, but made no use of it. Long before then, however, zinc was produced in India. Later it was produced in southern China. Possibly the Chinese obtained their knowledge from India. The Chinese in remote places still produce small quantities of zinc. I have seen photographs of their furnaces; or pots, for they hardly deserve the dignity of being called furnaces. I imagine that they are the same that were used centuries ago, for I cannot conceive of anything more primitive.

Anyway, it is certain that the idea of a commercial production of zinc in Europe was imported from the Orient, where the metal was known in commerce as Speauter and Spiauter, whence speltrum and finally our term spelter. Tutanego and Tuteneague are other old names.

Dr. Isaac Lawson went to China about 1730, expressly to discover the method of its production. What connection there was between Isaac Lawson and John Champion we do not know, but the latter obtained in 1739 a patent for a process of distillation downward and at some time between 1740 and 1743 erected a works at Bristol and actually began the manufacture of spelter. A production of 200 tons per annum is mentioned. In about the year 1766, Bishop Watson visited the Champion works and saw the process in operation, which previously had been

---

Manuscript received at the office of the Institute July 21, 1936.

* Consulting Engineer, New York, N. Y.

kept rigidly secret. This was the process of distilling a mixture of ore and carbon in a sealed clay pot, from the bottom of which a tube projected downward, letting the vapor condense in it and the metal drip into a basin. Dr. Percy saw one of these furnaces in operation in 1859. They were then considered rare. What is most amazing is that any of them should still have been in use at that time; and equally amazing is that one of them should have been built in New Jersey during the '50s.

In 1758 Champion obtained a patent upon the extraction of zinc from blende, including the roasting of blende. By that time, therefore, all the fundamental features of the process of getting zinc from its ores, both oxide and sulphide, were known and practiced. In 1805 Hobson and Sylvester at Sheffield discovered that zinc could be rolled if it were heated to 100° to 150° C.

Toward the end of the eighteenth century, Johann Ruhberg, a metallurgical operator of Pless, in Silesia, is said to have learned the art of zinc distilling in England, which may be authentic inasmuch as the beginning of zinc distilling in Silesia evinces distinct traces of British origin. In 1798 Ruhberg constructed a furnace at Wessola, utilizing the pots of a wood-fired glass furnace. For raw material he used zincky crusts from an iron blast furnace. In 1805 Karsten studied the process at Wessola and introduced the use of calamine. The results were so encouraging that in 1808 the Government built the Lydogniahuette at Königshuette. During the next 10 years other plants followed in rapid succession. The original glass pots gradually took the form of semicylindrical muffles. The first plant of Georg von Giesche's Erben at Scharley had a furnace with four muffles. The gas and vapor emerged from the top of the charge instead of from the bottom, as in the British prototype, but they passed downward through a knee-shaped condenser, which survived for a long time in Silesian practice, and the spelter dripped into a pan, from which it had to be remelted, just as from Champion's original furnaces.

About the same time that Ruhberg was beginning at Wessola, Bergrath Dillinger was building a zinc furnace at Döllach in Carinthia, and was exhibiting some original ideas, by employing small vertical pipes for the distillation. These pipes were so petty, being about 40 in. high and about 4 in. in diameter, that their capacity for charge was small, and the use of the Carinthian furnace never spread nor survived very long, although as late as 1840 it was still in use. It was a process utterly incapable of commercial development, but it gave the idea of retorts heated all around and also the idea of a vertical setting of them, which led not a few subsequent designers to try to practicalize it, all of whom were unsuccessful through failure to understand physical principles until recently, but neither the Roitzheim-Remy furnace nor the New Jersey furnace can be considered outgrowths of the old Carinthian.

The invention of the Belgian process of distilling is classically ascribed to the Abbé Daniel Dony, who by tradition was ordered by Napoleon I to find a way of making zinc, obeyed orders and by means of a flowerpot accidentally attached to a reverberatory furnace found that zinc was condensing in it, received a concession of the mines of Moresnet, March 24, 1806, and so on; all of which is legendary, except the concession, and not very probable. It is possible that Abbé Dony was experimenting, but that he was inventing is doubtful. He obtained a patent (Dec. 7, 1809) for a zinc-distilling furnace, but in it there is nothing suggestive of what subsequently became known as the Belgian furnace. The first description of a Belgian furnace was given by Hollunder in 1818, who described from observation a furnace of this type at Stolberg, and by hearsay one at the St. Leonard's works at Liége. The Stolberg furnace exhibited all of the essential elements of this type. Who was its designer is unknown.

From this review, we may date the occidental, commercial production of zinc from about 1739. We may then jump ahead about 100 years to see what had been commercially accomplished. There are no statistics of production in Great Britain prior to 1855. We may conjecture that in 1837 it was producing at the rate of about 2500 metric tons per annum. In that year, according to Neumann, the production of Germany (chiefly Upper Silesia) was about 11,000 tons, of Poland about 2200, of Carinthia about 100 and of Belgium about 1800, a total for Europe of about 17,600. The predominance of Silesia and Poland (their metallurgical districts being in proximity) is striking. We are told that their product was largely consigned to India and China. Europe itself had not yet learned to make much use of zinc.

In 1836 distilling was begun at the Heinrichshuette at Stolberg, near Aachen, and there was then introduced a form of furnace, subsequently prevailing in the Rheinland and Westphalia, that was a compromise between the Belgian and the Silesian and was known as the Belgian-Silesian or the Silesian-Belgian, according to the predominant characteristics. Those terms long ago passed out of use, the early composites being gradually molded into a distinct type that eventually came to be recognized as the Rhenish. In the early compositions the retorts followed the muffle shape of the Silesians, but they were of less height, and while the lower row sat on the hearth an upper row bridged from shelf to shelf. The condensers extended from the retorts in direct line, as in the Belgian furnace, but they were enclosed in deep closets after the Silesian fashion. The retorts were banked in double tiers in an undivided combustion chamber. Thus, the Silesian thoughts predominated. Gradually, however, three rows of retorts were provided, all of them bridged, and the retorts changed in cross section from muffle shape to elliptical, the furnace leaning thus more towards the Belgian.

At the present time the Silesian furnace has practically passed out of use and we have only the Belgian and the Rhenish. As between them I find it difficult to express a sharp distinction. The use of cylindrical retorts, or retorts of elliptical cross section, with their rear ends supported on ledges of a middle wall and their front ends supported in a shallow devanture, would unhestitatingly be pronounced Belgian. A furnace with large elliptical retorts, with their rear ends supported by a grill, or banquette, in a single combustion chamber and their forward ends supported on ledges in a front wall divided into deep closets, would be unqualifiedly described as Rhenish. We find, however, some Belgian furnaces with large retorts and some Rhenish furnaces with a middle wall and are uncertain how to describe them.

In the early days of the art the ore to be distilled was commonly calamine. In Upper Silesia it was of relatively low grade and the basic conception was quantity and low cost of treatment. In Belgium it was high grade and there was more consideration of percentage of metal extraction. The Rhenish metallurgists had high-grade ore and aimed toward a compromise between cost and recovery.

From 1840 to 1860

About 1840 the methods of zinc distilling in Upper Silesia, in Rheinland, in Belgium, and in Wales (where the Vivians had begun in 1835) had become fairly well settled. The 20-muffle furnace created by Knaut in 1833 had quickly become generalized in Upper Silesia. Dominique Mosselman, who had entered upon the management of the industry in Belgium and had promoted it with great enterprise, had died in 1837, being succeeded by his son, who organized the Vieille Montagne company, which then had the works at Liége (St. Leonard's) and a newer plant at Angleur, the latter destined to become the nucleus around which this famous company grew. From 1840 to 1860 there was no noteworthy improvement in the art. The great concern of everyone was the economical combustion of fuel, the construction of furnaces that would stand up for a campaign of reasonable duration, and the manufacture of retorts that would be reasonably durable. A great worry was the enormous consumption of coal per ton of ore, which early established the principle that for the beneficiation of zinc ore it must be carried to the coal, rather than the coal to the ore. No one then knew much about how to burn coal efficiently, and metallurgists were everywhere groping. This was perhaps a reason why almost every works had its own design of furnace, and why even at the present time there is a broad diversity of forms in use in European practice. It would run away with my space if I should enter upon a description of all the furnaces that were introduced, and the details of practice with them. This has been done with conscientious care by Lodin in his "Métallurgie du Zinc."

Up to about 1860 there was no great improvement in the art. The furnaces were increased in size, especially as to number of retorts, without making any material change in their dimensions. The Silesians obtained an increased number by extending the hearth area. The Belgians did it by increasing the number of rows, getting up as high as nine, which passed the limit of ability to charge from the floor and necessitated the use of a platform. The smelters were worried by the fragility, porosity and other defects of their retorts, which were laboriously made by hand. They were also worried by high coal consumption. Direct firing was the common practice, first on plain grates, later on step grates, and eventually with under-grate blast of air. Many experiments in respect of distilling cycle were made, ranging from 12 to 36 hr., with a gradual settling down to 24 hr. The knee form of condensers continued in use in Upper Silesia.

An attempt to distill zinc for spelter was made in the United States at Newark, N. J., in 1850, ore from northern New Jersey being charged into Belgian retorts just as it came from the mines. Owing to the high tenor of the ore in iron and manganese, leading to excessive breakage of the retorts, the attempt failed. In 1856 the Lehigh Zinc Co. erected a distilling furnace of the Silesian type at its mine near Friedensville, four miles south of Bethlehem, Pa. This also was a failure. In 1856 F. W. Matthiessen and E. C. Hegeler, who had just come to the United States from the Bergakademie at Freiberg, Saxony, experimented with New Jersey ore, but soon they diverted their attention to the zinc deposits of Wisconsin and late in 1858 began the erection of works at La Salle, Ill., which was selected as the point where the Illinois coal field approached nearest to the Wisconsin mines. The works at La Salle went into operation in 1860 and have continued without interruption to the present time. In 1859 Joseph Wharton built for the Lehigh Zinc Co. a Belgian furnace for treatment of the Friedensville ore.

In 1869 the Glendale works were built at St. Louis to treat calamine from southeastern Missouri, and in 1870 the Illinois Zinc Co. built at Peru, Ill., to treat ore from Wisconsin. When the Joplin ore came into the market in 1873, numerous small plants were built in the vicinity of Pittsburgh, Kansas. All of these early American plants were built with small, direct-fired Belgian furnaces, their design being substantially as in Europe.

While in the metallurgy of zinc in the United States from 1850 to 1860 there was a good deal of bungling in the process of learning how, which was being done by men without scientific training, except Matthiessen and Hegeler, there occurred one invention of the first order in importance. This was the grate of cast-iron plates with small conical perforations, the smaller diameter at the top, introduced (or adopted) in 1851 by Samuel Wetherill. In connection with the muslin-bag apparatus, invented by

Samuel T. Jones, for the collection of fume, there was evolved what has ever since been known as the Wetherill process, or the American process, for the production of zinc oxide directly from ore. Several persons participated in the evolution of these ideas, which were coincident and collaborative, but the name of Wetherill became attached to both the furnace and the process, and we need not be any more analytical.

The Wetherill is a process of reduction of zinc oxide by carbon, distilling the zinc and immediate burning of the vapor. The Wetherill furnace is in effect a large retort in which with the aid of an under-grate blast of air coal is burned internally and reduction of zinc oxide and immediate combustion of zinc occur in the deliberate abstention from maintaining the reducing atmosphere that is essential in the closed retort. This process was put into use at the Passaic Zinc Works in Jersey City in 1854, and has been in use in many plants in the United States ever since. In Europe, it has found scarcely any application.

If, starting from the primitive English and Silesian practices of zinc distilling, the introduction of the cylindrical retort of small diameter, bridging the combustion chamber at a small angle from the horizontal, heated all around, and connecting with a condenser from which spelter could be drawn molten, was the first great invention in the metallurgy of zinc, it seems to me that the invention of the Wetherill process was next in order. The numerous improvements in distilling practice, such as increase in number of retorts, modification of the daily cycle of operation, betterment of furnace construction, etc., were mechanical details rather than anything of major progress in principles. The groping for better art in the combustion of coal was not peculiar to the zinc industry, for the same needs and applications existed with respect to the glass industry and others in which a high and uniform temperature is necessary.

A historical review of the pyrometallurgy of zinc is rendered difficult by the diversity of practice among individual works, especially those of Europe, and the persistent retention of old methods. In this respect the pyrometallurgy of zinc has differed sharply from that of copper and lead. In copper and lead the introduction of new methods has quickly become general, and old plant has been scrapped. In zinc, on the other hand, there are to be found some plants that are modern and others that within themselves exhibit more or less a history of the art. A few years ago I found a small plant in Wales that was still using the furnaces of the middle of the last century; and a major plant in Belgium that had some halls equipped with one of the most superb of the modern gas-fired furnaces, and other halls equipped with direct-fired furnaces of 50 years in age. In this review, therefore, it is impossible to generalize practice, for the reason that there has been no such thing, and I may only review progress in knowledge and experience that might have been generally adopted. In American practice we have had more generalization than in Europe, but we also have had diversity and a common reluctance to surrender old plant.

The world's production of zinc had attained considerable proportions by 1860, in which year the outputs, in metric tons, were as follows: Germany, 55,359; Austria, 1,301; Belgium, 22,027; Russia (Poland), 1,838; France, 124; Great Britain, 4,427; Spain, 1,853; total 86,929. No production was reported for the United States. If there were any, the quantity was negligible. It is noteworthy that the largest production was still coming from Upper Silesia, where it was derived entirely from calamine, distilled in retorts that had the old knee-form condenser, which were used in furnaces that did not have a chimney to draft them. The first chimney in the district was built in 1861, at Lipine.

From 1860 to 1880

Prior to 1860 there had been some ideas of gasification of coal as a means of producing a long flame and fireplaces had been taking the form of boxes containing a deep bed of coal, becoming in effect partly gas producers, and there were also some ideas of preheating the secondary air expressed in the Boetius, or Mentzel-Boetius, producer, but it was not realized that preheating air by causing it to pass through channels in the walls of the producer or in those of the combustion chamber of the furnace was robbery of heat rather than recuperation. Soon after 1860, however, sound ideas began to obtain. Between 1865 and 1870 furnaces with a central burner and an independent gas producer were introduced in Upper Silesia and were in common use by 1875. In 1866 R. Wabner at Lipine introduced a furnace that had beneath its hearth tubular recuperators around which the wasting heat escaped and through which air was forced by a blower. Although this furnace was called a success, the management of the works presently abandoned it. As we now examine the specifications, we appreciate that the proportions were pitifully inadequate. However, this was the prototype of a class of furnace that was in later years to be of some importance. About contemporaneously with the Wabner furnace in Upper Silesia, the Siemens regenerative furnace was being introduced at Auby, in the north of France, and proved a failure. In 1878 the same furnace was introduced at Peru, Ill., where it survived and became the forerunner of one of our standard American types. In Europe it became established at the Birkengang works at Stolberg and throughout Germany it is a furnace, or furnace principle, extensively used at the present time.

The period from 1865 to 1875 appears to have been an era of experimentation, especially in the direction of gas-firing. There were many practical obstacles. Refractory material was not good. Heat-exchanging flues cracked. Retort breakage was heavy. Checkerworks clogged with zinc oxide and coal ash. The gas producers were clumsy and inefficient. There was no very good knowledge of thermodynamics and so on. A retarding influence was the idea that the gas producer ought to be a part of the furnace; that the sensible heat of the coal gas ought to be preserved. If the producer was built as a separate integer, as in the Siemens furnace, it was commonly too small or ill suited to the coal that was to be gasified. It was the invention and introduction of our modern, mechanical gas producers that really made the gas-firing of zinc-distilling furnaces completely successful.

During this period there was occurring at La Salle, Ill., a line of experimentation and development that was to be of profound effect upon zinc distilling, especially in American practice, which proved partly to be good and partly to be bad for us. Edward C. Hegeler, whose fame in American annals ranks with that of Samuel Wetherill and John Price Wetherill, had been, like everyone else in this country, distilling with direct-fired Belgian furnaces. In the effort to increase their capacity, row after row of retorts had been added until the number had risen as high as nine. With such furnaces a man can charge from the floor only five rows. To go above that a platform had to be moved up, upon which the charge was thrown from the floor and thence into the retorts, which of course was awkward. Hegeler conceived of building a long furnace like a tunnel, putting the gas through it horizontally instead of from the bottom upward, which was in effect like building a high, narrow furnace and turning it over upon its side. In later years Mr. Hegeler described his idea to me in about those words. This also opened the way to a good deal of mechanization. A track could be laid in front of the furnace, and on it could be put a car carrying the charge, from which the charge could be shoveled directly into the retorts, also a car to assist the men in raking residues out of the retorts, a ladle car for drawing spelter, etc., all of these cars being shielded against the heat of the furnace and making the work easier for the men. It permitted, moreover, of a different organization of labor, which was regarded as superior, and anyway was more economical. Instead of a section of furnace being attended by a squad of three men, performing all the work, the long furnace was manned by a large crew of which groups performed special operations.

Hegeler's first large furnace was erected in 1872 and had 408 retorts (204 per side). This furnace had many peculiarities that were abandoned in later constructions, but the general principle has remained unchanged. At La Salle the length of the furnace was increased finally to 1008 retorts, but that was found to be too much and the number was reduced to 864. For a good many years the Hegeler furnace was used only at La Salle.

By 1880 the several forms of distilling furnaces had become well differentiated and well developed. In Kerl's "Grundriss der Metallhüttenkunde," second edition, 1881, are descriptions of most of the types of furnace that are in use today, though naturally improved in details, structural and thermal. The Belgians had their simple direct-fired furnaces, built double (back to back) with a grate under each bank of retorts. Also the Hauzeur furnace, used at Auby, in which the flames drew over the middle wall and descending through a bank of retorts escaped in such a way as to afford some heat recuperation. The Angleur furnace, similar in principle to that at Auby, but gas-fired instead of grate-fired, was built as a massive comprising 400 retorts. The Loiseau furnace at Ougree, also gas-fired, also resembled the Hauzeur furnace. The Hauzeur furnace, let it be remarked, followed at Auby the trial there of the Siemens regenerative, and was a thoroughly intelligent conception. In the Rheinland the three-row Rhenish furnace had already assumed a nearly definitive design, although the lowest row of retorts still sat on the hearth and the Mentzel-Boetius firing was still employed. At the Birkengang works a countercurrent recuperative furnace with 226 retorts was in use in the same plant with Siemens regenerative furnaces. At the Muensterbusch works, also at Stolberg, there were recuperative furnaces designed on the principle of Gaillard & Haillot, with 240 retorts. The Birkengang and Muensterbusch furnaces outlined quite fully what was 20 years later to be developed in the Convers & DeSaulles furnace at Palmerton. Birkengang distilled a ton of roasted ore (or calamine) with 1.2 ton of coal In Upper Silesia there were simple gas-fired furnaces and Siemens regeneratives of effective design. The art of gas-firing, together with the realization of economy in fuel, had gone a long way in Europe between 1871 and 1880.

In the United States there were nonregenerative gas-fired furnaces at La Salle and the Siemens furnaces of the Auby type at Peru, but in Kansas and Missouri all of the furnaces were then direct-fired Belgians of small size, and wasters of fuel, whose chimneys were torches to be seen from afar on the prairie at night. In the east at Jersey City, Newark, Bergenpoint and Friedensville there were similar furnaces, but better built, with Wetherill grates and sealed ashpits, so that an under-grate blast would promote the combustion of anthracite fines.

In both Europe and America practice had become standardized, especially in Europe, where many of the later refinements were already in use. Everybody had settled down to the 24-hr. cycle in distilling. Retorts of elliptical cross section had displaced those of circular cross section at Angleur and elsewhere in Belgium. A proportion of coke was introduced into the batch to graphitize them. The Dor press had been adopted at Ampsin (in 1872). At Auby an addition of 1 per cent of sodium chloride was made to the charge, not to improve the extraction of zinc but to reduce the formation of blue powder in the condensers Furnace campaigns lasted as long as three years. Mechanical mixing of the charge had been introduced in some plants.

A subject that was much engaging the attention of zinc metallurgists at this time, especially those of Upper Silesia, was imperfect condensation of the zinc vapor. The Belgian metallurgists had early extended their clay condensers by attaching to them a cone or canister of sheet iron, effecting a prolongation that in American vernacular is called simply a "prolong." The Rhenish metallurgists had done the same thing. The Silesians, on the other hand, had stuck to their old knee-form condenser until 1860. When they changed over to a straight-extending condenser they found themselves limited as to its length, for they had the practice of charging the retort with a long spoon through the condenser, and its length was substantially restricted to the depth of the embrasure or closet in which it was set. The great retort might then deliver more vapor than the limited condenser could handle. We see pictures of the simple Belgian prolong attached to a Silesian retort, but we also see pictures in the literature of 1871–1880 of many complicated forms, whence we may deduce that the subject was worrying. In my own experience, I have never seen a retort of 2-cu. ft. capacity, charged with high-grade ore (60 to 65 per cent Zn) to the densest degree to which a simple canister prolong did not effect complete condensation, giving a gas flame free from any trace of zinc. In American practice we have not generally used prolongs, for the reason that with our more costly labor the additional recovery of zinc does not pay for putting them up and taking them down, which with the Belgian furnace must be done every day. However, the Silesians solved their condensation problem in a different way, as presently I shall describe.

In looking backward we may see that the zinc distillers of Europe had already in 1880 a fairly good practice. They were quite ignorant of the principles of physical chemistry, for that science had not yet been born. They were not very analytical and comparative in respect of their accounts, wherefore it is rather difficult from old records to ascertain just what they were accomplishing. They were still making retorts by hand, or in some instances by the augur machine, and they were not very good. They appreciated the advantage of gas-firing with heat recuperation for their distilling furnaces, but they did not have any good *gazogenes*, as the French call them, or gas producers, as we say. The Siemens producer was not a good one and the early condemnation of the furnace at Auby, which subsequently became successful at Peru with gas from a Taylor producer, may have been in part ascribable to that. The art of blende roasting, on the other hand, was distinctly backward.

In 1880 the production of spelter reflected the strong progress in the art that had occurred since 1860. Production in 1880, in metric tons, was as follows: Germany, 99,646; Austria, 4,310; Belgium, 59,880; Russia (Poland) 4,390; France, 16,332; Great Britain, 7,279; Spain 4,221; United States, 21,080; total, 217,138. The American production of zinc at this time was chiefly by the western works. The production of the eastern works was probably not more than 5000 tons.

From 1880 to 1900

The zinc specialists of the '80s had also adventured into the field of hydrometallurgy. The ingenious Parnell process had been applied on a considerable commercial scale in Swansea for the beneficiation of mixed sulphides from a mine in Algeria (1879–1883). At Langelsheim and Oker, in the Lower Harz, the mixed sulphide ores of that ancient mining district were heap-roasted and so sulphated that much of their zinc could be leached out, giving a solution of zinc sulphate that could be crystallized out, affording a product pure enough to be used for lithopone manufacture.

The backwardness in blende roasting up to 1880 may have been due to its relative unimportance. Outside of the United States the ore supplies were principally of calamine, and the calcination of such ores to reduce their weight prior to shipment was commonly practiced at the mines, an art that now has substantially vanished. Even with the increasing use of blende, it often was received first at chemical works for the manufacture of sulphuric acid, as at Baelen in Belgium and at the Rhenania works at Stolberg, and the calcines were thence passed on to the distiller. So was it that some distilleries had no roasting equipment, and for many years the figuring in Europe was on the basis of calamine or calcines, whereas in the United States it has always been on sulphide ore, or raw ore, or green ore, except in New Jersey and Pennsylvania.

The roasting furnaces in use up to 1880, and in the United States for 20 years after that, were in the main the long two-hearth Freiberg *fortschaufelungsofen*, rabbled from two sides, and the multihearth shelf burner in which the ore was pulled forward on the topmost hearth, pushed backward on the next, and so on. In the United States the shelf burner was preferred. Occasionally it was built above the distilling furnace and the waste heat from the latter was caused to pass through it, but this was not considered the best of practice, for the timing of the two operations—roasting and distilling—did not naturally coincide. With the beginning of utilization of blende-roasting gas for manufacture of sulphuric acid both the *fortschaufelung* furnace and the shelf burner were muffled, so that the gas from the roasting chambers would be undiluted by the gas from the firebox. While these were the standard means for desulphurizing blende, there were introduced here and there new contrivances, some of which heralded improvements to be generalized many years afterward. Thus the Gerstenhöfer furnace, introduced at Frieberg in 1863, which I saw in use there in 1893, was the primordial form of our tower furnaces and the suggester of the pure idea of shower roasting, which Stetefeldt two decades later exposed more fully. The Ross and Welter furnace that was used at Oberhausen about 1880 was a clear forerunner of our modern McDougall.

Soon after 1880 there was a striking development in roasting furnaces. Edward C. Hegeler in 1881 built at La Salle the huge, mechanically rabbled muffle furnace that is known by his name and began the manufacture of sulphuric acid. From that time until about 1925 it was the only furnace used in the United States for blende roasting for acid manufacture, and it is still so used at Rose Lake, Danville and Hillsboro. During this period it experienced mechanical improvements, but it has remained essentially as described in 1881. It is an immense massive of brick masonry, of great capacity, costly to build, only semimechanical, gas-fired, and not very economical in operation. Some years ago we made a survey of its sulphurous gas at hourly intervals during several days and were shocked at the disclosure of its poverty at the best and at its irregularity. According to academic rules we should not have been able to make acid from it very successfully, but we did.

In Europe the development in blende roasting in the '80s ran toward the perfecting of the old muffle furnaces and so there were evolved the Hasenclever, the Eichhorn-Liebig, and finally, as the last word, the Rhenania. These furnaces, especially the Rhenania, were superb exhibitions of the mason's art. Their walls were thick, for the conservation of heat, and the rabbling doors were small and tightly closing for prevention of leakage of air into the furnace. Of the three hearths only the lowest was muffled in the end, for it was learned that the self-heat of the burning blende produced on the middle hearth a higher temperature than gas burning in flues under it could do. The idea in the roasting furnaces of this type was to produce a gas of high tenor in sulphur dioxide, a desulphurization down to 1 per cent S or lower, and the minimum use of extraneous fuel.

In other branches of the art there was progress during the '80s. The hydraulic press for making retorts under great pressure, which had been invented by Emile Dor at Ampsin in 1872, came into extensive use in Belgium and Rheinland. In Upper Silesia the Kleeman condenser, with which the escaping gas was caused to pass through a bed of incandescent coke, was introduced. It was troublesome to keep in order, but it obtained extensive application and I saw it in use in 1893. A more general adoption that was almost contemporaneous, and eventually was the supplanter, was the Dagner condenser, which consists of three fireclay sections, laid one above the other, with communicating holes so that the gas and vapor has to zigzag through them and travel a relatively long course. This continued in general use until the Silesian process itself passed out. With the Silesian furnace it was mechanically easy to cause the gas from the closets to pass through a main flue. Trials of this proved, however, that such collection was not worth while.

Even by 1890, or soon afterward, the production of blende by the mines of Upper Silesia was so much increasing, and its tenor of zinc was so much higher than that of the calamine, that the old furnaces were becoming unsatisfactory. At the Guidottohuette there were built furnaces with two rows of smaller retorts in about the same way that the Belgian-Silesian method developed in the Rheinland half a century earlier, but although they excited interest they did not immediately inspire extensive imitation.

By 1890 the art of zinc distilling in Belgium, France and Germany had become well developed. Rhenania furnaces were used for blende roasting and sulphuric acid was commonly made from the sulphur gas. Roasting was done to about 1 per cent S with the use of as little as 12 per cent coal and a tenor of SO_2 in the roast gas as high as 7 per cent. Retorts were made by hydraulic press out of a well compounded batch of fat clay, chamotte, coke dust with perhaps an addition of silica if the nature of the ore indicated the desirability of acidity, and the formed retorts were carefully seasoned. Retort life was about as high as it is now. There were good ideas as to the compounding of ores to counteract slag formation, and high-iron and high-lead ores had lost their terrors. In the West prolongs were used on the condensers; in Upper Silesia the Dagner condenser was employed; either way condensation was good. Extraction of zinc in distilling attained fairly high percentages, though not as high as we realize now. Retort residues were jigged to concentrate their lead, or if sufficiently rich in silver the entire residue might be passed on to the lead-smelting blast furnace. Leady spelter was refined by remelting and settling out the lead, which also equalized the composition of the spelter.

Coal consumption was not as low as it is now, charging of retorts was not so dense, the percentage of reducing coal was higher, charging was still done extensively through the condenser, and there were other details to be improved. New designs of furnaces were introduced here and there. Among these especial mention should be made of the Welzer, built at Overpelt about 1893, which was a Siemens regenerative furnace with the gas and air reversing back and forth in the combustion chamber in parallel with its longitudinal axis instead of up and down in parallel with the tranverse axis as in the Auby furnace. This was a distinct development of idea, especially in a practical way. The Welzer furnace continues to be one of the forms extensively used. In respect of the reversing regenerative furnaces we may catalogue the original Siemens, or Auby; the Welzer; and the Dor, or Dor-Delattre. All others are merely minor modifications of these prototypes. At about the same time with the Welzer there began to be designs of furnaces in which only the secondary air was preheated, the gas being brought from the producers with as much as possible of its original heat, which was of course a rational conception.

In respect of most of this we knew as much toward the end of the '90s as we do now, although we could not compute quite so well.

About 1890 much attention was devoted to the treatment of mixed sulphide ores, which previously had been treated only for the production of zinc sulphate in the Lower Harz, for the production of zinc oxide for subsequent distilling by the Parnell process at Swansea (1879–1883), and tentatively by other methods elsewhere. The new attention was inspired by the great occurrence of mixed sulphide ore at Broken Hill, New South Wales, and by the approaching exhaustion of the carbonate ores at Leadville, Colo., leaving the sulphides. Schnabel had been at Broken Hill, and had made a scholarly report on the subject, without offering any solution. I had been working on Leadville ore with hydrometallurgical thoughts. The metallurgical treatises of the time told me to roast sulphatizingly, but I found that impossible other than for an unsatisfactory proportion. I though then of roasting the ore sweet, with the idea that the zinc oxide would be entirely soluble in sulphuric acid, but to my surprise I found that solubility was poor at the best. Increasing the strength of the acid and prolonging the digestion accomplished nothing more than gelatinizing the silica and producing an unfilterable liquor. I reasoned that there must be formed in the roasting an insoluble compound of zinc, and could thing of nothing else than a compound of zinc oxide and ferric oxide, which I called zinc ferrate. Prof. H. O. Hofman was skeptical of this, but he was finally persuaded to experiment and produced zinc ferrate (or zinc ferrite, as he called it) synthetically. I mention this episode because the subject subsequently became of such tremendous importance in electrometallurgy.

Soon after 1880 there was put forward an idea of which we did not contemporaneously appreciate the importance and indeed did not learn to do so until 35 years later. This was the invention of the sulphate electrolytic process of Léon Létrange, which was described in a German patent of July 8, 1881. Létrange obtained a solution of zinc sulphate by leaching roasted ore. He electrolyzed the solution, using insoluble anodes, among which he suggested lead, and for cathodes proposed zinc or copper. The solution was purified before electrolysis. The spent electrolyte enriched in sulphuric acid was used for the digestion of more ore. Herein lie the major elements of the modern electrolytic zinc process. Létrange experimented in a little plant at St. Denis, near Paris, and obviously encountered many practical difficulties. However, he exhibited specimens of cathodes at the World's Fair in Chicago in 1893, and thought that he had then overcome his difficulties, but probably he had not.

George Nahnsen obtained patents on a process that was substantially the Létrange, and experimented with it at Lipine in 1893. I conversed with him and saw something of his work at that time. As we look back to his old specifications we can see that he had good ideas as to chemical and physical conditions. He introduced zinc-dust purification and prescribed the correct conditions in respect of degree of purification (or almost so), advisable current density, circulation of electrolyte, etc. There were many other experimenters in this field during these two decades, many of them appreciating the exigency of solution purification, but no one then understood just what was meant by purification and how refined it had to be. Following Nahnsen, E. A. Ashcroft led the Sulphide Corporation into the building of a costly plant at Cockle Creek, New South Wales, for the commercial treatment of the mixed sulphide ore of Broken Hill, which was then one of the great metallurgical problems. The Cockle Creek plant proved to be a dismal failure, not so much by reason of false theory as by reason of impractical development. Anyway this threw a wet blanket over the idea of electrolytic zinc extraction for a good many years.

Among other things the pioneers were obsessed with the fallacy that a hydrometallurgical, electrometallurgical process would be a means for beneficiating the mixed sulphide ores as they come from the mines. In later years we learned that the electrolytic process, which is inherently costly, called for an enriched concentrate, rather than for low-grade ore.

Mention should of course be made of the Hoepfner process for the electrolysis of a zinc chloride solution that was being developed contemporaneously and was put into practical use at Führfurt-am-Main, and by Brunner, Mond & Co., Ltd., at Winnington, in England. By this process chlorine was liberated at the anode, and by utilization for chemical products, which could be done in a chemical factory, the cost was divided between two commercial products—chlorine and zinc. The Hoepfner process continued in use at Winnington through a rather long series of years, affording an annual production of about 1000 tons of high-grade spelter.

Apart from this groping into hydrometallurgy and electrometallurgy, the commercial and technical developments of this decade, especially in the United States, were so diverse and so important that it is difficult to summarize them without wandering afield. We had the development of superior rolls for fine crushing, first designed by S. R. Krom and glorified by Philip Argall, who wrote a treatise on the science of fine crushing with rolls, prior to which no one knew anything about the subject. In 1896 A. R. Wilfley introduced his famous shaking table as a means for mineral separation, and contributed immensely to the ability to concentrate difficult ores. John Price Wetherill invented his ingenious method of magnetic separation, which made minerals of low magnetic quality susceptible and separable, and solved the previously troublesome problem of separating the willemite and franklinite of the Franklin and Sterling mines. This was improved mechanically by Lewis G. Rowand. August Hecksher brought together the conflicting interests in those mines, causing them to be absorbed into the New Jersey Zinc Co., and ending a litigation that had been troublesome for about 50 years. In 1895 natural gas was discovered at Iola, Kansas, and Robert Lanyon with his brother decided to use it for zinc smelting there. H. C. Meister in 1893 applied the Brown horseshoe roasting furnace to blende roasting at Collinsville, Ill. B. F. Hobart and A. B. Cockerill consolidated many of the small smelteries in Kansas and Missouri into the Cherokee-Lanyon Spelter Co. This gives a long list of things about which to think.

In entering upon the utilization of natural gas, Robert Lanyon imitated the long Hegeler furnace at La Salle, blind to the difference between producer gas and what was substantially pure methane, and simply introduced the gas into one end of the furnace, providing a blower to supply air along the furnace through branches from a longitudinal main above it, this being similar to the equipment of the furnaces at La Salle. Other builders at Iola, which quickly became an important metallurgical center, ignorantly followed suit. The conception of firing with natural gas was very seductive, for a supply could be obtained by putting down a 4-in. well right in the smeltery yard, with but little piping to the furnace, and the cost of gas was not more than 3¢ per 1000 cu. ft. However, as late as 1900 much trouble was experienced from dissociation of hydrocarbons in the combustion chamber, which sometimes clogged with carbon the spaces between the retorts and simply reflected ignorance of the proper burning of this powerful fuel. Consequently, although the cost of smelting per ton of ore was much less than in the coal-fired Belgians that were being used concurrently, the extraction of zinc was so much less as to be quite offsetting.

At this time zinc smelting in Kansas and Missouri was conducted mainly by rule of thumb. No works had a chemist, and the practice generally was atrocious. The charge was still mixed on the furnace floor, the charging of seven-row and eight-row furnaces was done from a platform, retorts were made by boring, and in some plants by hand even at this late date. Ores were bought by guess rather than by assay. And so on.

This would be, however, an incorrect indictment of American zinc-distilling practice in general. The metallurgists of New Jersey were scientific men, including George C. Stone and George G. Convers, who had developed a good practice with the use of anthracite coal, and were then (in 1898) beginning the construction of the great Palmerton plant in which all of their experience and improved ideas were to be embodied, including the excellent Convers and DeSaulles countercurrent recuperative furnace, which was probably the highest development of that type. S. C. Edgar, at Cherryvale, Kansas, in 1899 built an excellent plant, with short furnaces rather than long ones, free from all the fallacies that prevailed at Iola. The U. S. Zinc Co. built a costly plant at Pueblo, Colo., duplicating one of the most modern plants (Overpelt) in Belgium, using the Welzer furnace. The Matthiessen and Hegeler Zinc Co. at La Salle and the Illinois Zinc Co. at Peru had developed their respective practices to an efficient degree.

From 1900 to 1915

In Europe, G. Welzer, who managed Overpelt from 1891 to 1894, in 1896 entered the employment of the Counts Henckel von Donnersmarck in Upper Silesia and remained with them as chief manager until 1903, during which period he introduced the Rhenish method, together with the Welzer furnace, and achieved full success whereas all previous efforts had failed. After this the old Silesian process gradually faded away, but I saw it in use at Paulshuette, preserved more or less as a curiosity, in 1928.

The Dor-Delattre furnace, which in Belgium is now used at Rothem, Budel, Flone and Valentin Cocq, in France at Auby, in Spain at Aviles and in Germany at Duisburg, was patented in 1905. The Folliet furnace, in use at Corphalie and Boom, is merely an imitation of the Dor.

In the United States, the Kansas smelters, other than Edgar, were not to remain backward very long. In the course of a few years chemists and metallurgists were added to their staffs. Otto Rissmann was one of the most thoughtful and most lovable among them. Mechanical mixing of the charge, at first in a clumsy way, was introduced. Mechanical furnaces were adopted for roasting—the Brown, Pearce, Wethey and Zellweger all being tried—but the Ropp became the favorite. The distilling furnaces were reduced from six rows high to five, and even to four. They were repiped so that gas could be burned in sections of their fronts on the Bunsen burner principle, and were otherwise improved. The long furnaces comprising 800 retorts were in some instances separated into two of 400, with the general tendency that way. So was developed what we may call the Iola type of furnace, from its origin in that place. Iola was a great metallurgical center, but with the exhaustion of its gas pool, a good one while it lasted, it faded away.

It is proper to refer to the additions to metallurgical literature that occurred about this time. There was my own treatise on the "Metallurgy of Zinc and Cadmium" that was published in 1903 and has the distinction of being the first treatise devoted entirely to this subject appearing in any language. This was soon followed (in 1905) by the erudite and monumental work of A. Lodin on "Métallurgie du Zinc." Emil Günther brought out "Die Darstellung des Zinks auf elektrolytischem Wege" in 1904. Liebig's "Zink und Cadmium" appeared in 1913. It may be thought that these contributions to technical literature helped some in the advancement of the art. Anyway, I have been told as much.

The idea of the Hegeler furnaces, which was ingenious in 1870 and had long been successful at La Salle, afforded a precedent in gas-firing, in respect of which knowledge was low, whereas the Siemens furnace at Rich Hill and Pittsburgh (at the old Granby works) had failed, and the builders of new works naturally wanted to stick to something that had been proved. Yet, the Hegeler furnace was inherently defective in principle. As I pointed out in my treatise in 1903, the execution of combustion in a tunnel of indefinite length would come to the point where there would be no combustion owing to excessive dilution of the gas with its own inert products. So was it that at La Salle a length was reached from which there had to be recession. In our most modern forms of this furnace, reduced to temperate length, say 76 retorts per row per side, with the best possible adjustment of admission of secondary air section by section, there is a tremendous drop in temperature from the gas inlet end to the chimney end, and this is detrimental in several ways to best results in distilling. Moreover, the manual labor is not performed to the best advantage in front of a flaming wall 80 ft. long. This is not a peculiarity of the Hegeler furnace, for the Neureuther-Siemens is also very long. The difference in conditions in respect of human comfort between our long American furnaces and the types of furnaces used in Europe is impressive. It has been my observation that monthly records in European practice are more uniform than in American, where we commonly experience what is called the summer slump. I have been inclined to associate this with the greater severity of our physical conditions, being mindful also of the naturally higher atmospheric temperatures that we have, especially in the Midwest.

The same organization of labor and mechanization can of course be enjoyed with a row of short furnaces, end to end, as was appreciated at Cherryvale in 1899 and later at Iola when the long blocks were divided, and there is also the advantage that the maneuver is shortened and the time of the distilling period is correspondingly lengthened.

As the Iola gas pool waned and as the trend of the Mid-Continent oil and gas field was traced southwestward into Oklahoma, zinc smelteries were built all along that line. There soon began to be, however, a feeling that supplies of natural gas were uncertain and ephemeral and that for the creation of a permanent metallurgical industry it was better to move eastward, whither the spelter had to go anyway on its passage into consumption, and where the utilization of the sulphur in the ore could be made in areas affording a market for sulphuric acid. Consequently we had erection of new plants, most of them coal-fired, at East St. Louis in southern Illinois, at Hillsboro, Danville and Depue in northern Illinois, at Terre Haute in Indiana, at Langeloth and Donora in western Pennsylvania, and at Clarksburg, Meadowbrook and Moundsville in West Virginia. Clarksburg and Meadowbrook were able to obtain a supply of natural gas. Most of these plants were designed for the manufacture of sulphuric acid and were provided with Hegeler furnaces for blende roasting. For distilling, gas-firing from coal, we had settled down to two types of furnaces, the Hegeler and the old Auby-Siemens, of which the latter had been slightly modified by Charles F. Neureuther, superintendent at Peru, and had become known as the Neureuther-Siemens. Nobody thought of trying anything else, not even the good furnaces that had been introduced at Palmerton and Pueblo. Our builders were essentially imitative. An engineer experienced at La Salle when commissioned to build a new plant naturally followed the lines with which he was familiar. Thus, for example, Langeloth built in 1914 was simply an exalted La Salle, while Donora designed soon afterwards by the same hands was an improved Langeloth.

As we entered the twentieth century we became prepared for some great events, which were to have a profound effect upon our zinc industry and its metallurgy, if not to revolutionize it. In 1905 I was commissioned by the Canadian Government to study the zinc resources of British Columbia and the beneficiation of its ores. In this my principal colleague was Philip Argall. Reference may be made to our report published in 1906 (Report of the Commission on the Investigation of the Zinc Resources of British Columbia). In this it is of record that we measured and sensed the Sullivan as the great mine of the province, but did not know how its cryptocrystalline ore could be separated into commercial minerals. As our report was on the eve of going to press I heard of successful flotation of zinc blende in Australia and caused some experiments to be made with Canadian ores, with promising indications. The commercial introduction of the froth flotation process dates from about this time. It gave a new supply of high-grade sulphide ore, brought the Broken Hill zinc ore bountifully into the market, and in the United States brought in the Butte & Superior ore. Important as were those events, the froth flotation process was for a good many years limited to relatively simple separations.

On the subject of ore supplies a digression is here in order. We had been taught by geologists that zinc was the most bountiful of metals, for the reason that with depth many of our mines became more and more zincky. Nevertheless, about the beginning of the present century we began to experience a distinct shortage of ore. Within a few years this was ameliorated by digging up the dumps of zincky tailings that had been accumulating at Leadville, Colo., since 1886; by the discovery that deposits of calamine in the Leadville mines had been overlooked in the misconception that they were simply limestone; by the discovery that the mineralization of the Joplin district extended into Oklahoma with more importance than ever before; and by the proper preparation of the Broken Hill ore. Metallurgically this not only endowed zinc smelters with new ore supplies, but also it put an end to the age-old problem of mixed sulphide ores and direct beneficiation of them, for if they could be concentrated mechanically that was a cheaper way of getting rid of worthless gangue than any chemical method could possibly be.

The Period of the Great War

The Great War had an instantaneous and powerful effect on the metallurgy of zinc. The ore of Broken Hill, which by that time had become a major supply, had been going mainly to metallurgical works in Belgium and Germany, whose metallurgists had become the most expert in its beneficiation. At once these outlets were cut off, with the result that the British had plenty of zinc ore and nowhere to smelt it. This led to a demand upon the United States to supply spelter, and stimulated both the opening of new mines and the erection of new smelting works. Even the old Belgian furnaces of Pittsburgh, Kansas, which had been practically on the scrap heap since about 1901, when they had been unable to meet the competition of natural gas, were revamped and restored to ephemeral production. The U. S. Steel Corporation built its great plant at Donora in the shortest time of record for such a construction. Contracts were made for bringing an immense quantity of Australian concentrates to this country for smelting. Our metallurgists had no difficulty in treating them.

The phenomenally high price for spelter that prevailed in 1915–1916, and the wide margin between spelter and zinc in ore, was really an invitation for the provision of additional metallurgical capacity, and offered full cognizance of the uncertainty of the future and the exigency of reckoning plant amortization in as short a time as a year. Under the inspiration of such an invitation the metallurgists of Trail and Anaconda, who had plenty of zinc ore available but no chance for its beneficiation in the ordinary way, were led to turn their thoughts to electrolytic extraction, and the old Létrange process. Ever since the failure at Cockle Creek, nearly 20 years prior, electrolytic experiments had been going on here and there, without exciting much attention or enthusiasm. The economic conditions of 1915, however, made it attractive to take a chance on anything reasonable. S. G. Blaylock was the prime mover at Trail and Frederick Laist at Anaconda. Both became immediately successful, meeting with many difficulties but mastering them one after the other. Several small electrolytic plants subsequently sprang up, at Park City, Utah, at Keokuk, Iowa, and other places, but they died soon after the end of the war, when the economic conditions in zinc settled down.

An enterprise was then born, however, which survived. This was the bold conception of H. W. Gepp, now Sir Herbert Gepp, of transporting Broken Hill ore from Port Pirie (the port of shipment) 1200 miles by sea to Risdon, Tasmania, where cheap hydroelectric power was available for contract by transmission 65 miles. In the development of this successful enterprise I am proud to have had some part.

The Risdon adventure was noteworthy in a good many ways. In the preliminary testing of the ore, which was done first in New York and later at Bully Hill, Calif., great trouble was experienced in plating the zinc, owing to an impurity that was eventually ascertained to be cobalt, wherefore means for cobalt purification had to be devised, this being a major difficulty from which Anaconda and Trail had been free. The first Risdon plant was a 10-ton unit, laid out on a plan to multiply units as experience was gained. But it was quickly ascertained that the economic advantage of the electrolytic process was largely in the concentration of operating, and that 10 units of 10 tons each were unprofitable, while one of 100 tons might be profitable. So the first plant was scrapped after a brief operation and a new 100-ton plant was instituted. Risdon was one of the first plants to receive its current from a distant source and change alternating current to direct current by means of rotary converters. The new plant was completed in 1923.

As a digression, it may be usefully remarked that the association between Australian and American metallurgists that began at this time led to the great development of lead smelting and refining at Port Pirie, and subsequently through the same financial group the taking over of the zinc-smelting industry of Great Britain (where the great plant at Avonmouth had been built during the war) and improving its metallurgical practice so that it became the equal of any on the Continent, and perhaps in some respects superior.

The war created a demand for zinc for the manufacture of cartridge brass, which required a high grade of spelter, wherefore the refining of Prime Western by redistilling was instituted on a large scale in Kansas and Oklahoma. Thus could be produced metal of something like 99.9 per cent fine, but of course all cadmium could not be eliminated. When the United States entered the war such metal could not meet our ordnance specifications, which could be met by only two producers. All of the others united in engaging me to study this problem, in which was involved what I had previously characterized as the cadmium myth. In this study I had the valuable assistance of the late W. H. Bassett. My finding was, in brief, that prior failures of cartridge brass by season cracking were due to something other than the presence of cadmium and that even if a high-cadmium spelter were used for the manufacture of brass all of the cadmium would be eliminated in the process of brass-making. The arguments were so convincing that the ordnance specifications were summarily changed and redistilled Prime Western spelter was furnished in great tonnage for the manufacture of American ammunition, just as it had been previously for British, French, and Russian, and no fault ever was found with it. Apart from the commercial interest of this episode, it intimates how slight was the knowledge up to this time of the effect of impurities in spelter or alloys with zinc. No one had dreamed of such a thing as specifying 99.99 per cent Zn for any purpose.

The Great War inspired some researches in respect of the properties of zinc. It launched the electrolytic production of zinc. It stimulated the electrothermic production of zinc in Sweden. It led to the building of many new plants on the ordinary lines. When the war demand ceased, we found that we were everywhere overbuilt, outside of Belgium, and ere long many of the new plants had to be scrapped and written off. In Belgium most of the zinc works strung along up the valley of the Meuse had been seriously damaged, as had Auby, in the north of France, and all of these were promptly rebuilt. This deserves a remark upon the remarkable survival of zinc smelting in Belgium, which once could draw from the famous mine in Moresnet, but long since ceased to be a producer of zinc ore of any consequence. The continuance of the industry reflects skill in the art that has come down from generation to generation. We used to think that this was so valuable an asset that any undertaking to institute zinc smelting in a new country would be hazardous. However, we have seen such attempts consummated successfully in Australia (Port Pirie), in Japan, and in Mexico (Rosita), and have become converted to the belief that the training of a new personnel is not impossible and may possibly be beneficial.

Since 1920

The depression of 1920–1922 threw a wet blanket over the zinc industry, but once that had ended plans began to crystallize for the erection of zinc electrolytic plants in many parts of the world. Without attempting to enumerate them in chronological order, there were erected plants in Japan, Italy, France, Northern Rhodesia, Poland and most recently at Eitrheim, near Odda, in Norway, at Flin Flon in Manitoba, Canada, and at Magdeburg in Germany. Of these plants the two in Poland and the one in Germany use coal as a source of power. All the others use water power. Silver King, in Idaho, and Evans-Wallower, now idle, at East St. Louis, use the Tainton high-density process. Magdeburg uses a compromise. All of the others use the ordinary low-density process.

It is fitting here broadly to discuss the economics of the electrolytic process of zinc extraction. Its applicability in the early days was a function of the reasonable correlation of three factors; viz., good zinc, solubility of the ore, a substantial tenor of by-products (silver and lead) in the ore, and cheap hydroelectric power. Another factor is the ability to produce a high grade of spelter, which may command a premium. During the war it commanded a large premium. In 1922 there was no premium. In recent years there has been a moderate premium.

These elemental factors continue substantially at the present time, but with some modification. Thus, high zinc solubility is not so important as originally, for in smelting the residue for its lead content, its zinc passes into the slag, from which it may be burned out, which is now a matter of commercial practice. Cadmium has been added to the list of important by-products. Of all the by-products the electrolytic process yields nearly 100 per cent, while in distilling practice the recovery of them is practically much lower, although not so necessarily.

I have hereinbefore remarked that one of the exigencies of the electrolytic process is its application to large-scale production, this being most distinctly a requirement under American conditions, where, at least in our Northwest, a plant to produce 20,000 tons of spelter per annum is probably the irreducible minimum. Under foreign conditions, where general expense is not so heavy, where the wages for labor are lower, etc., smaller plants appear to be commercially operative. Nevertheless an examination of the list will show that most of the zinc electrolytic plants of the world, except those in Italy and Japan, are of upward of 20,000 tons annual capacity.

The growth in electrolytic zinc production has been in part through the treatment of ores that might have been transported elsewhere for distilling, e.g., the production at Risdon, Eitrheim, Szopienice and Magdeburg, but it has been largely through: (1) the beneficiation of ores occurring in remote places where no coal is available and whence the freighting of ore would be prohibitive; (2) the beneficiation of ores from which the recovery of by-products, perhaps from the purchase of custom ores, pays the bill. This is a broad generalization, as to which no doubt some exceptions may be noted. However, in American practice we have seen two plants at St. Louis treating the same kind of ore and the distilling plant outrivaling the electrolytic plant; and we have seen straight zinc ore produced in the extreme Northwest pass by the electrolytic centers there, and go all the way to St. Louis. In Upper Silesia the two methods appear to be about equal in respect of the cost of producing a pound of zinc.

Contributory to the great development in the metallurgy of zinc that occurred during the '20s was the invention, or improvement, of the process of preferential, or selective, flotation. We had previously been able to make two-mineral separation, but were embarrassed by three-mineral separation and complex cases generally; also in respect of some of the worst instances of cryptocrystalline mixtures. My first observation of the marvelous separation of the difficult ore of the Star mine in the Coeur d'Alene was at Kellogg in 1922. I had previously had a problem in connection with ore from the Saxberget mine in Sweden, that was being smelted at Trollhättan. While it was being concentrated by flotation in Sweden the enrichment was not very high. I sent a parcel of the ore to flotation experts in Arizona, who were unable to accomplish anything better than was being done in Sweden. After seeing what was being accomplished at Kellogg I sent a parcel of the ore to the experts there. They immediately reported ability to make a very clean separation. Whether from Kellogg, or from elsewhere, the news of the new technique spread rapidly, and by 1926 we began to have new ore supplies, enriched in zinc to a high degree, coming from mines in many parts of the world. Reference to the statistics, which on this subject are very good, show that the great tonnage of blende concentrate derived from mixed sulphide ore has been raised to 50 to 60 per cent zinc and reduced in lead to 0.5 to 3 per cent.

Flotation concentrates in immense tonnages introduced new problems for the distillers, especially those of the United States, most of which are situated at great distances from the mines and operating on a custom basis, requiring many handlings. This was more of a problem in the United States, where the handling of ore through the plant is done mechanically and on a larger scale than in European plants, where the tonnages are less, the handling more gentle, and the use of shovels and wheelbarrows more extensively surviving. At least, such was my contemporaneous observation.

When the flotation concentrates were first received in Oklahoma, in roasting on single-hearth Ropp furnaces, not making sulphuric acid, and mixing with coarser ores, we managed to get along, incurring more of a dust loss than was comfortable. When, however, these ores began to come to eastern plants, for roasting in multiple-hearth Hegeler furnaces, the dusting became prohibitive, not only owing to physical loss, which rose to a staggering figure, but also owing to inability of the plant personnel to labor in an atmosphere so dusty. This led by force of circumstances to a complete revision of the ore-handling and roasting methods in most of the major American plants. Before describing this, however, I should refer to the introduction of the sintering process, almost contemporaneously.

The idea of sintering calcines from the blende-roasting furnaces originated with Gilbert Rigg, who put it into commercial application at Port Pirie in 1917, where zinc distilling was still being done. Rigg roasted the ore down to about 9 per cent sulphur, then mixed with it a proportion of green ore and fed it to a Dwight-Lloyd sintering machine, igniting the bed at the head end, executing the classic sulphate-sulphide reaction and effecting almost complete desulphurization, at the same time fritting the ore into a cake. This became, therefore, an autogenous roasting, desulphurization being effected by self-burning, except for a very small quantity of oil required for ignition. In almost any good roasting furnace the blende would self-burn down to 9 per cent sulphur. Besides effecting this, the physical condition of the ore thus desulphurized was so improved that it reduced more easily than unsintered calcines and gave a higher percentage of zinc extraction.

The results reported from Port Pirie were so astonishing that at first they were received with some incredulity. Before we got ready in this country to turn seriously that way experiments were instituted by the Vieille Montagne company at Baelen, Belgium, with the difference that there the ore was first dead-roasted and then was mixed with about 6 per cent of fine coke and thus sintered, this becoming known as the Baelen, or Bellefroid, process. It introduced the fear that there might be some unwelcome prereduction of zinc oxide and volatilization of zinc.

In Europe the Rigg process was introduced at Seaton-Carew in 1921. In 1923 Otto Rissmann introduced it at Bartlesville, Okla., and in 1924 it was pronounced as being beyond the experimental stage. This installation was followed by one at Collinsville, Okla. In 1925 sintering was begun at Avonmouth and at Arnao (Spain). About the same time a pilot plant was installed at Langeloth, but the decision in the end was in favor of the Baelen process. All subsequent introductions in the United States followed this lead. There remained perhaps a certain Rigg flavoring, inasmuch as a little sulphur as sulphate was left in the preroasted ore, but not enough to result in material loss of sulphur or let the gases be a social nuisance.

In the revision of American roasting practice that began in 1927 and was pretty well completed in 1928–1929, the old Hegeler furnaces were discarded in favor of furnaces of the McDougall type. Rose Lake and Donora adopted the Herreshoff furnaces, 12 hearths high at Rose Lake and 16 at Donora, but Langeloth adopted furnaces from the design of M. F. Warner and myself, in which the wall was built of exceptional thickness, in which cooling air was positively forced through a central column and stirring arms, but in reverse direction from the ordinary, and in which there were means to redistribute preheated air among the several hearths of the furnace, following the thought in my U. S. Patent 786567, of 1905. The ore was dried on top of the furnace and spilled over into a gutter, from which it was fed mechanically into the first hearth and into one or more of the hearths below it. The idea was to conserve heat, transfer it from places where there was a surplus to places where there was a deficiency, and so effect autogenous desulphurization, which was substantially accomplished. The Langeloth furnaces were 12 hearths high. Similar furnaces were later built at Rosita and at Magdeburg.

The Langeloth installation differed from others also in that whereas they were provided with Cottrells as scavengers of dust and fume, at Langeloth the furnaces were drafted by exhausters through Whitmore Siroccos, the idea being to return collected dust directly into the furnaces where originating. Whether of the best conception or not, it is the fact that Langeloth has for seven years made sulphuric acid by the chamber process with no other means for purifying the roaster gas.

As regards mechanical handling, it was found that if the flotation concentrate, received as a stiff mud, containing about 10 per cent water, were dried down to about 4 per cent, it could then be put through the preliminary processes without dust loss and could be carried by inclined conveyor belt to the tops of the roasting furnaces, on which drying could be completed. From the roasting furnaces the calcines went through coolers, etc., in a closed circuit. The dust loss was in these ways reduced to small proportions.

The revision in American ore-handling and desulphurizing practice that was thus made at Langeloth, Rose Lake and Donora cost about $1,250,000 per plant, perhaps somewhat more at Donora. Other plants adopted furnaces of the McDougall type, sinterers, etc., but none so extensively as the three just mentioned.

The next step in blende roasting was the development of shower roasting at Trail, where the interior hearths were removed from a Wedge furnace and the ore was showered down, burning in a flash. We have seen that the idea of shower roasting was first suggested in the old Gerstenhöfer furnace. In our 12-hearth and 16-hearth McDougalls there is a good deal of the shower effect as the ore falls through their numerous drop holes. The high efficiency of those furnaces is largely ascribable to that. The culmination of the idea at Trail is interesting in many ways. Apart from the great increase in furnace capacity and the perfect control over the desulphurization, there are no hearths to be barred for removal of accretions, no rabble arms to be replaced and no doors to be opened, letting in false air, and less power to operate. On the other hand, there is the penalty of a large dusting, to be subsequently collected outside of the furnace.

Shower-roasted calcines have been used with great success for lixiviation at Trail. They have been used by the Illinois Zinc Co. for sintering for distillation in the old way. They have been used at Meadowbrook by the Grasselli Chemical Co. for briquetting for distilling by the New Jersey continuous process. These form, therefore, a wide variety of application. Nevertheless we are not yet sure that the process is a general substitute for prior methods of roasting, being conscious of trouble with it that has been experienced with some ore. Some ores may require regrinding after drying to make them fine enough and some ores may have a gangue that leads to building up in the bottom of the furnace. Consequently, we should hesitate about adopting it in a new plant in the absence of trial of ore, and this might be a deterrent in the instance of a custom plant that is bound to receive many ores.

CONTINUOUS DISTILLING

The old Carinthian furnace, with its vertical retorts, inspired many thoughtful metallurgists to try to practicalize its idea. One of these constructions was that of Binon and Grandfils, which was tried at Stolberg about 1880. The Chenhall furnace, which was also introduced about

1880 and is referred to in the technical journals of that period, was never used practically, nor was the Keil furnace, described in 1888.

The early inventors along those lines overlooked the difficulties of hanging of the charge, of the inability of gas and vapor to work out through a column of fine ore, and the physical principle that in distilling a charge of zinc ore and carbon we must get through with preliminary reactions prior to active distilling, else we shall condense the zinc too largely as blue powder. The same natural difficulty baffled the electrothermic distillers.

Just prior to the beginning of the Great War the Roitzheim-Remy furnace, with vertical retorts, was said to be promising great things, trials having been made at Oberhausen (Hamborn) in 1912. It passed out of sight but returned again into view in 1925, following the installation of a plant with five furnaces, each of 22 retorts (11 per side) at Niederschöneweide, a suburb of Berlin. Later a furnace was erected at Bensberg and one at Avonmouth, both of which were condemned after brief operation.

The Roitzheim-Remy retorts are of annular cross section, about 22 in. in inside diameter and about 6 ft. high. Inside of the retort, which is externally heated, is a central tube into which the gas and vapor of distillation pass through apertures, from which communication is made to a large condenser projecting horizontally from the furnace. The interior construction is complicated and the furnace is costly to build. Its use at Niederschöneweide, which continues, is confined to the distilling of galvanizers' skimmings and ashes. When a retort becomes defective it is lost until the furnace is rebuilt. Apart from that drawback, it is a continuously working furnace, ore being charged into the top and residue withdrawn from the bottom.

The Roitzheim-Remy furnace was followed by the New Jersey process of continuous distilling in a vertical retort, which is not to imply that the New Jersey process was in any way an outgrowth of Roitzheim-Remy experience it being rather an outgrowth of experience with briquetted charges in the manufacture of zinc oxide. The New Jersey process will be described in a subsequent monograph in this volume (p. 427), wherefore I shall confine myself to broad comments. The use of carborundum retorts gave good conduction of heat and permitted the retorts to be made unusually wide; viz., 12 in. The introduction of the charge as briquettes preserved large interstitial spaces, permitting internal convection and radiation of heat and affording easy egress for gas and vapor. Previous coking accomplished the condensation of zinc vapor as spelter, free from the oxidizing action of carbon dioxide, the gas escaping from the condenser being under 1 per cent carbon dioxide, which matches the gas from the horizontal retort at its best.

Another continuously operating vertical retort is that of Gaskill, commercialized by the St. Joseph Lead Co. at Josephtown, Pa. At

Josephtown the retorts are circular in cross section, 60 in. in diameter, and 22 ft. high between the electrodes. Inasmuch as the heating is internal, developed through resistance of the charge, a large diameter is permissible. The charge is sintered and carefully sized, so as to have free interstices and permit the escape of gas and vapor. The latter is burned immediately upon issuance from the furnace and the zinc is collected as oxide. So far the Josephtown furnaces have been used only for the production of oxide. (See p. 599.) It is believed that they may be adapted to the condensation of spelter, but that has not yet been commercially accomplished.

The idea of distilling zinc in an internal, electrically heated retort is about as old as the idea of the electrolytic process, going back to the '80s. About 1901 a good deal of work on this line began in Sweden, especially by Dr. Gustav DeLaval, and elsewhere in Europe. Some of the early ideas were sound; others were manifestly unsound and impracticable.

There was a common disregard of the principle that zinc ore cannot be distilled continuously without prereduction without an excessive condensation of zinc vapor as blue powder. Also there was a disregard of the principles of lead smelting and zinc smelting involving widely different thermal conditions, and the idea of tapping molten lead and molten spelter from the same furnace was held to be chimerical. Finally, it was felt that electrothermic smelting is an expensive way of getting rid of the gangue of the ore. We learned in the course of time that the consumption of current in making slag was about as much as in reducing the zinc; moreover, that in making an easier melting slag it carried away zinc, just as in lead smelting, and zinc extraction either as spelter, as powder or as fume was relatively low.

In 1903 a company was organized to exploit the DeLaval process and commercial plants were built at Trollhättan, Sweden, and Sarpsborg, Norway. In 1909 Trollhättan had nine ore-smelting furnaces, each of 350 hp., and in 1913 it had 18 furnaces, each of 500 hp. In that year the production of spelter was about 2100 metric tons. During the war four more furnaces were added and the production rose to between 8000 and 10,000 tons per annum. In five years, 1916–1920, about 50,000 metric tons of ore were smelted, yielding nearly 20,000 tons of crude spelter. The bulk of this production occurred in 1916–1918. In 1924–1930 production was at the rate of about 5000 tons per annum. Early in 1931 production ceased. Since then there has been no electrothermic furnace in use for the production of spelter anywhere in the world, so far as I know.

The early Trollhättan furnaces were single-phase, with bottom contact and one movable top electrode. Each furnace connected with its own brick-lined condenser and zinc was obtained partly as spelter and partly as blue powder.

Toward 1920 some larger furnaces were built, with improved electrical operation, and the original idea of trying to condense zinc directly as spelter was abandoned. In the new practice the furnaces were operated at higher temperature, all of the zinc and lead was volatilized and condensed as blue powder, and the gangue was drawn off as a highly siliceous slag, about 50 per cent silica, which had the advantages of reducing dilution of the ore with fluxes so as to make anything like a singulo-silicate slag, and also reducing the quantity of zinc entering the slag and with it to be carried away and lost.

The condensed blue powder was re-treated in a rotary furnace, electrically heated, in which the oxidized skin and sprouts on the particles of zinc (globular under the microscope) were rubbed off, so permitting them to melt down, this being the ingenious process of Mr. Cornelius, who was metallurgist at the plant. From the Cornelius rotary furnace, leady spelter was tapped. This was refined by redistilling in a third, electrically heated furnace.

Consequently the Trollhättan metallurgists came around to recognition that the distilling of zinc from ore is necessarily a two-stage process, which may consist of (1*a*) prereduction and (1*b*) distilling for spelter; or (2*a*) distilling for blue powder and (2*b*) re-treating the blue powder for spelter.

The Cornelius process for treating blue powder was, of course, quite different from the old Montefiore process, used in the early days of zinc metallurgy on the Continent, in which the blue powder was melted down under pressure, compelling the zinc particles to coalesce and naturally producing a spelter so contaminated with zinc oxide that it would be useless under present commercial conditions and probably was objectionable in the olden days.

Direct Zinc Oxide

Along with the beginning of the production of spelter in Missouri and Kansas, several small plants for the direct manufacture of zinc oxide, or of leaded zinc, from the low-grade calamines were built here and there. Scarcely anything remains known in respect of their experiences, which probably were ephemeral and unimportant. The first noteworthy adventure in this field was the beginning of production (in 1882) at Mineral Point, Wis., in which the brothers D. B. and T. D. Jones were leaders, and the outgrowth of which was the Mineral Point Zinc Co., now a subsidiary of the New Jersey Zinc Co. In this plant the original installation was of the Wetherill furnace as used in the East, but gradually this was modified until there was created a distinct western type. Who was the author of this is unknown, but W. C. Smith had much to do with the development of it.

At the plants in New Jersey and Pennsylvania the Wetherill furnaces were individual units, although built together in a block, and from each one, or each grate, the products of combustion were piped separately to the main exhaust, the control of blast and exhaust being individual.

In the western furnace a block was divided transversely into a series of grates, arched over, but opening into a large overhead chamber, through which the products of combustion were drafted. Differences in the working of individual grates were thus equalized and operating conditions were less rigid than in the eastern furnaces. The two types of Wetherill furnaces are now distinguished and described as the Eastern Wetherill and the Western Wetherill.

In 1907 an important oxide plant was built at Coffeyville, Kansas, and since then there have been plants at Canyon City, Colo., Leadville, Colo., Hillsboro, Ill. (1920) and Columbus, Ohio (1920). The production of zinc oxide and of leaded zinc (zinc oxide plus lead sulphate) in these western plants has attained large proportions. At most of them the Western Wetherill furnace is used.

Apart from the introduction of the Western Wetherill furnace, the Wetherill process experienced but little change for 50 years. About 1903 charging from overhead was introduced at Palmerton, but this, like other improvements in the process up to that time, was only of mechanical nature. The great improvement in the manufacture of zinc oxide directly from ore occurred in 1920 when the metallurgists of the New Jersey Zinc Co., among whom J. A. Singmaster was instrumental, conceived the idea of briquetting the charge, making it up into briquettes of double-pyramid shape. This immensely simplified the handling of the furnaces besides improving the extraction of zinc. Whereas with a loosely mixed charge the furnaces had to be operated under seal and there were constant occurrences of the air blast breaking through the charge bed and forming craters, with the briquetted charge combustion could be performed with open doors, the briquettes burning like anthracite coal on an open grate in a domestic fireplace, effecting the reduction of zinc oxide in the open. The operation was easier on the grates and there were other advantages, but of course the cost of briquetting was considerable.

From the burning of briquetted charge on stationary grates the transition to a traveling grate, continuously working, was a natural thought. This had long been an ideal. As far back as 1910 some tentative experiments toward adaptation of the Dwight-Lloyd traveling grate (as used in the sintering machine) with updraft for this purpose had been made, and about the same time J. A. Singmaster suggested a tunnel type of furnace through which the grates were to be carried on cars. The standard Coxe stokers used for burning coal in steam-boiler practice also offered a suggestive precedent. In preliminary trials along these lines one difficulty proved to be the formation of blowholes along the sides.

The introduction of the briquetted charge abolished all trouble in that way, and the mechanical Wetherill furnace of large size and capacity naturally followed. In 1924 the New Jersey Zinc Co. had six such furnaces in operation, treating 300 tons of ore per day. With no great difference in the proportion of coal per ton of ore as compared with previous practice, the intimacy of contact by virtue of briquetting and the regularity of conditions by virtue of mechanical operation resulted in increase in the percentage of zinc extraction and, of course, saving of labor.

The Wetherill process in its purity has been confined to the direct manufacture of zinc oxide of commercial quality. Similar processes, using the same means for filtering the smoke, but designed to make only an impure oxide as a metallurgical between product, as a means for concentrating zinc were early introduced. F. L. Bartlett, first at Portland, Me., and later at Canyon City, Colo., in the late '80s and early '90s used a form of Wetherill grate for this purpose and smelted the clinkered residue in a low-blast furnace, collecting the fume from both. Bartlett was distinctly a pioneer in the treatment of mixed sulphide ore, by burning out their zinc. R. G. Hall, at Florence, Colo., much later smelted in a reverberatory furnace, collecting copper matte and fuming off the zinc. His zinc fume was subjected to electrolytic extraction at Keokuk, Iowa. Pape, in the Lower Harz, burned off zinc in a grate kiln and produced zinc fume for subsequent metallurgical treatment.

All of these processes were suggestive, but none of them amounted to much for commercial use; perhaps owing to imperfect mechanization, perhaps because a real need for them had not yet arisen. In metallurgical theory the genesis of all of these processes goes back to the original Wetherill invention.

A great development in processes of this kind occurred about 1925, following two important conceptions, neither of which was really new. One of these was the introduction of the Waelz furnace—a long, revolving cylinder much like the revolving cement kiln—in which a mixture of zinc ore and carbon is burned so as to expel the zinc from the ore. The requirement for carbon is relatively small, because after the utilization of its energy for the reduction of zinc oxide the burning of the zinc vapor gives back a corresponding quantity of energy right in the furnace, where it is needed. The other important development was that the residues from zinc-leaching (electrolytic) plants having been passed on to lead smelters for extraction of their lead content, silver, etc., with the natural production of a zinc slag, the latter could be resmelted economically with further addition of carbon, for expulsion of its zinc.

The Waelz process, which was developed in Upper Silesia in 1923 and was commercially applied in 1925, is a relatively cheap method for the concentration of zinc from low-grade ores, especially calamines, and is extensively used for that purpose all over the world. The dezincing of slags in various forms of cupolas and other furnaces is also now practiced extensively, especially as an appendage to electrolytic extraction. It is possible, therefore, to bring the ultimate extraction of zinc up to nearly 100 per cent, although of course additional costs are incurred in doing so. The residues from Great Falls, Trail, Viviez, Baelen and Magdeburg are thus beneficiated. A great accumulation of zinc slag at Port Pirie, New South Wales, awaits similar treatment.

It is naturally desirable to extract the maximum percentage of zinc from any ore by leaching, but imperfect solubility of zinc, through the formation of zinc ferrate, which was long a drawback in electrolytic extraction, is not so important as formerly, inasmuch as undissolved zinc may be recovered by the scavenging process.

Under this head, mention should be made of the process of dezincing old brass junk that was introduced and highly developed at Carteret, N. J.

All of these processes for the recovery of zinc as oxide give a fume containing from 60 to 70 per cent zinc, its grade being run down by lead, which naturally fumes along with the zinc. Such fume is available for distilling for spelter, and for return to the electrolytic process, but in the United States it is largely passed on to the manufacture of lithopone.

Refining of Spelter

The refining of spelter has been practiced from early times, especially for deleading. In the distilling of lead-bearing zinc ore a certain proportion of its lead goes over with the zinc and condenses in the spelter. In remelting, lead settles out to a degree correlating with the temperature. In general practice it is possible to reduce the lead content to something like 1.25 per cent. This remelting has the further advantage of equalizing the furnace product, which, owing to variations in furnace temperature, will differ from section to section. Even if the spelter does not require deleading, it should be equalized for the sake of uniformity and the satisfaction of customers.

There has been no method for refining spelter by eliminating iron. However, high iron is almost always evidence of bad practice in distilling and handling.

Not until recently has there been any method of refining to eliminate cadmium, but inasmuch as cadmium comes over in the first part of the distilling operation, a classification may be made by keeping separately the several draws of spelter. Prior to the advent of the electrolytic process, all high-grade spelter was mainly a consequence of distilling selected ore, lead-free or cadmium-free, or both. In recent years there has been some practice in deleading and decadmiumizing ores, which may be accomplished in connection with the sintering process.

Apart from these methods, the refining of spelter until recently has been confined mainly to simple redistilling, but that does not succeed ordinarily in eliminating cadmium. During the Great War, Prime Western spelter was redistilled in immense quantity at works in Kansas and Oklahoma by the use of adaptations of the ordinary ore-smelting furnace.

During the same period crude spelter was electrolytically refined at Baltimore, Md., but the process was too costly to survive after the war.

It remained therefore for the New Jersey Zinc Company's process of reflux refining, an adaptation of fractional distilling, to accomplish perfect refining. This furnace was introduced commercially about 1934 and is now used in the United States, Great Britain, Belgium, Germany and Poland. As it is to be described in a separate monograph in this book (p. 445), no further remarks about it are necessary here.

SULPHURIC ACID

Although the manufacture of sulphuric acid from zinc blende overlaps into the field of industrial chemistry, reference to it properly belongs in this historical review. Zinc blende contains one unit of sulphur for each two units of zinc, and 2000 lb. of blende concentrates assaying 60 per cent zinc will yield close to 2000 lb. of sulphuric acid of 60° Bé. or 76.6 per cent monohydrate. Apart from the inherent value of the sulphur itself, zinc metallurgical works from early times existed in settled communities, wherein sulphurous gas could not be turned loose without creating a social nuisance and incurring pecuniary liability for damage. Consequently, when blende began extensively to replace calamine as the source of zinc, the metallurgists were forced to restrain the sulphur. The manufacture of sulphuric acid was the most practicable method, and the chamber process was at first the only one available. This was done in Europe during the '70s. In the United States, Matthiessen and Hegeler began to do it at La Salle early in the '80s.

The zinc smelters of Kansas and Oklahoma, situated in areas of relatively low economic development, wherein they neither do very much damage nor have any market for acid, waste their sulphur, except at Bartlesville, minimizing nuisance by dispersing it through high chimneys. The absence of a market for acid, or the glutting of a market, has always been troublesome to zinc smelters everywhere. It has been a common practice in Europe to consign the ore to one place for roasting and acid manufacture, and subsequently to transfer the calcines to another place for distilling. This has also been done in the United States, but not extensively. Owing to this economic procedure, many zinc metallurgical works in Europe include no roasting department; but in the United States practically all of our zinc metallurgical works are, and always have been, integrated.

About the end of the last century the contact process of making sulphuric acid, originating in Germany, was introduced at Mineral Point, Wis., and in 1906 Depue followed. When the development of petroleum refining in Oklahoma created a local market for sulphuric acid, Bartlesville began to make it and adopted the contact process. Later it was adopted at other plants. However, the great bulk of the sulphuric acid from blende roasting continues to be made by the chamber process.

Lithopone, Zinc Dust, Zinc Chloride, Et Cetera

In present practice the manufacture of lithopone, for pigment, etc., belongs distinctly to the metallurgy of zinc. This substance was first commercially produced in the United States by Cawley, Clark & Co., at Newark, N. J., in 1903. For a good many years it did not make much headway, but through chemical research that corrected some of its original defects, the industry went ahead by leaps and bounds, this having been especially noteworthy since 1920. In the earlier days the raw material was a variety of zinc products of more or less refuse character, but in recent years the lithopone manufacturers have turned to zinc sulphide ore, especially that from Oklahoma, as their raw material and have become competitive for it with the distillers.

The Oklahoma, or Tri-State, ore after dead-roasting has high zinc solubility, the formation of zinc ferrate in roasting being quite negligible. The lithopone manufacturers roast, leach and purify in just the same way in principle that the electrolyzer does, but having obtained a purified solution, the degree of refinement being more or less the same for either process, the lithopone manufacturer precipitates the zinc as sulphide by means of barium sulphide, whereas the electrolyzer plates it out as metal.

Of the same competitive nature is the recent process of "bethanizing" developed by Mr. Tainton, which in 1936 was commercialized on a large scale by the Bethlehem Steel Co. In this process the zinc from solution derived from ore is plated continuously on steel wires drawn through the cell, the steel being the cathode instead of the aluminum in the ordinary electrolytic process.

In a review of zinc metallurgy we must not overlook the important branch of reworking by-products, especially galvanizers' dross, skimmings and ashes, and miscellaneous junk, in all of which considerable skill is exhibited.

Galvanizers' dross in the United States is mainly distilled for spelter. This is done in the ordinary ore-smelting furnaces or in special furnaces having large, bottle-shaped graphite retorts, standing upright, or nearly so, the furnace being direct-fired. In recent years galvanizers' dross has been extensively distilled and condensed as powder, which is accomplished by sudden chilling in a large canister, the zinc precipitating as snow, so to speak, instead of as rain, as in the ordinary, hot condenser. The condensation of zinc in the prolongs of the ordinary condenser occurs as powder, and in Europe the commercial zinc dust is made as a by-product in that way. Zinc so condensed, however, has a certain oxidation of its globules, and in the United States the specifications for this product have been so severe that prolong dust could not be graded sufficiently high to comply with them. However, commercial zinc dust is seldom made directly from ore in the United States. In Europe galvanizers' dross is used extensively for manufacture of oxide.

Galvanizers' sal skimmings are redistilled in mixture with ore. They may be distilled alone, but their high chlorine, perhaps 4 per cent, causes that to be an unpleasant job. In the United States sal skimmings go mainly to the manufacture of zinc chloride.

Conclusion

One thing that must be especially striking in this historical review is the extent to which our ideas in present practice, in respect of which we are prone to pride ourselves, really date far back; and recognizing that our grandfathers had correct conceptions, much of what we have done has been to improve them and practicalize them by better mechanization, chemical and physical refinement, etc. Thus we have seen the idea of shower roasting not only outlined but also applied by Gerstenhöfer; the Auby-Siemens furnace designed, tried and condemned 70 years ago and now extensively adopted in both Europe and America; the electrolytic zinc process outlined by Létrange about 1880; and so on.

It is fitting to end this historical review with a summary of the state of the art at the present time, especially with reference to the old cyclic process. This is a difficult thing to do with any brevity, for the reason that so many survivals of old furnaces and old practices continue to exist, reflecting a peculiar psychology in zinc metallurgy upon which I have commented hereinbefore. Any idea of attempting to summarize all this would develop into composition of the order of a treatise. The only way out is therefore to confine ourselves to a summary of what may be considered as the best practice, with some distinction as between Europe and America.

Sintering Zinc Ores

By H. J. Stehli,* Member A.I.M.E.

The first sintering of zinc ores was done at the Bartlesville plant of the National Zinc Co., under the auspices of the late Otto Rissman. Mr. Rissman, who had had a long experience in the treatment of zinc ores, well realized all the difficulties of satisfactorily roasting zinc concentrates, which were becoming finer and dustier as each year went by—thus increasing the difficulties of roasting them in the existing forms of roasters, which were furnaces of the Ropp, Hegeler or similar types.

Mr. Rissman's idea of the advantages of sinter was expressed in this way: in a zinc ore dead-roasted in a mechanical furnace there are many particles that are just like an egg; that is, they have a hard and impervious film of fused material on the outside, and in the retorting this completely cuts off access of the reducing gases to the center of the egg until a temperature has been reached at which this shell of the egg can be broken down through fusion. A particle of sintered zinc sulphide, on the contrary, is exactly like a piece of sponge. The moment the retort reaches the temperature at which the reactions can take place, they begin, because the reducing gases have ready access to the interior of the particles by means of the pores of the "sponge." His faith in the advantages of sinter was amply borne out by the results obtained at the pioneer sintering plant for zinc ores installed by the National Zinc Company.

EARLY METHOD OF SINTERING

The method of procedure at Bartlesville was to roast the zinc concentrates down to somewhere in the neighborhood of 8 per cent residual sulphide sulphur; to cool these, then to wet them down to the proper moisture and mix them in the mixer of the sintering plant; then to sinter them by means of the heat available from the residual sulphides. The sulphur contents of the roast varied considerably, of course, as it was difficult with the furnaces in use to control the roasting exactly at any point short of dead roast. Hence at times the concentrates were roasted a little too low to sinter readily, and at such times the lack of sulphur was made up by the addition of raw concentrates to the sintering-machine charge in suitable amount.

Manuscript received at the office of the Institute Sept. 17, 1936.

* Metallurgical Engineer, New York, N. Y.

The resultant sinter was quite a different product from what sintering-plant operators had been in the habit of calling "sinter." It was very friable, because the Joplin concentrates being treated were nearly pure zinc sulphide, and contained only very small amounts of gangue matter; so that really the sinter made from these Joplin ores consisted of particles of zinc oxide stuck together by a thin film of fused oxide mixed with a very small amount of slag. In this sinter the shape of the original ore grains was retained to a considerable extent, and they could be seen with the naked eye when a piece of sinter was broken.

This sinter contained invariably a certain amount of partially sintered fines, which were high in sulphur, and it was necessary to screen the sinter to remove the unsintered high-sulphur particles if the clean sinter product was to be kept under 0.75 per cent sulphur. These screenings, of course, contained the high-sulphur unsintered fines, and also a very considerable amount of fine sinter, which, while low enough in sulphur, was of small grain size and therefore went through the screen with the unsintered fines.

When this material was returned to the charge it greatly assisted the sintering. The unsintered fines were of no particular value, but the sintered fines rendered the charge porous and open to the air blast; so that screening of the sinter became standard practice.

SINTERING ORES HIGH IN IRON

Only when ores are high in iron does a real sinter form, but as such a sinter is tied together by fused Fe_3O_4 rather than by silicates, the sinter is excellent and the desulphurization good, because fused iron oxide does not seem to glaze over the sulphide particles and retard roasting, as silicates do.

For example: hematite ore containing 5 per cent sulphur can be sintered down to 0.1 per cent sulphur without any difficulty, and the sinter will have a dense, fused structure. On the other hand, if a zinc ore contains large percentage of lead accompanied by silica, which makes very fusible compounds, the sinter will show the effects of fusion, and it will be difficult to sinter it down to a low sulphur content.

The Bartlesville plant was called upon to treat a large tonnage of a western concentrate, which was on hand and which had been very unsatisfactory when roasted in the old-type roasters. This concentrate ran high in iron, and when dead-roasted and retorted it very rapidly attacked the retorts and ate its way through them, causing high retort loss and high metal losses as well. This ore sintered very readily—more so than the Joplin concentrates. It made a harder sinter and one that bore more resemblance to the familiar sinter structure, but still had the characteristic fine pores—more like dry toast than like lead sinter, for instance. This sinter could be readily broken up to the size desired for the retort charge, somewhere between ¼ and ⅙ in., and caused the retort mortality to drop at once and the metal recoveries materially to increase. The sintering had performed something of distinct value in addition to eliminating the sulphur.

The reason that this particular ore when sintered no longer attacked the retorts probably lies in the fact that in the sintering fairly high temperatures were reached and rather infusible silicates were formed, from the excess of iron and the comparatively small amount of silica present; silicates having too high a formation temperature to permit of their being formed in the old-type roasters. Once, however, that the iron was partly satisfied by having been combined with some silica in the form of a high-melting-point slag, it had very much less tendency to attack the retorts, because in the retorts the fusion point of these slags was never reached, and only after reaching that point would they have a tendency to do damage.

Carbon as Fuel

The rather friable nature of the sinter, which is characteristic of practically all zinc sinters, was a distinct advantage—because, as stated above, material of ¼ or ⅙ mesh in size was wanted for the retort charge, and a sintered product like an average lead sinter, for instance, would have caused considerable expense in crushing to get it down to a suitable size for feeding to the retorts.

Because the physical structure of zinc sinter was such a distinct advantage in the retorting operation, the decision was soon reached that it would even pay to mix zinc ores that had been dead-roasted down to, say, 2 per cent total sulphur with fine carbon fuel and sinter the mixture. The product of this sintering behaved so much better in the retorts than the dead-roasted ore that it more than paid the cost of the additional operation, and incidentally a 2 per cent sulphur dead roast would generally contain a very large part of its residual sulphur as sulphate, which to the sintering machine was just as easy to remove as sulphide sulphur. So that the resulting sinter from this operation would contain as little as 0.2 or 0.3 per cent total sulphur.

One thing was very soon found; viz., that if a roasted concentrate containing anywhere up to 5 per cent residual sulphur was mixed in this manner with a suitable amount of carbonaceous fuel and sintered, the sintering machine had a capacity 50 to 100 per cent greater on such a charge than on a charge composed of concentrates roasted to 8 or 9 per cent sulphur, in which the residual sulphur alone was utilized to furnish the heat required for sintering.

The explanation of this is simple: the reaction in burning carbon to CO_2 evolves more than three times the number of heat units evolved in burning S to SO_2 and Zn to ZnO. The reaction of burning carbon produces much higher temperatures, and is more rapid and concentrated than that of sulphur, and this facilitates the reaching of the comparatively high temperatures required to desulphurize zinc sulphide and produce the necessary reactions that cause the formation of sinter from zinc ores.

It has already been pointed out (p. 38, this volume) that lead sulphides and zinc sulphides require entirely different sintering conditions. With the zinc sulphide, it is impossible to produce premature fusion, especially on ores like those from Joplin or Tennessee and Virginia, and the highest temperature that can be evolved in the sintering is the one that will give the best results. As carbon does this better than sulphur, it is a distinctly better fuel than sulphur for sintering zinc.

It was found that the shelf furnaces that were installed at most zinc works in recent years in place of the old reverberatories could roast the zinc concentrates down to about 5 per cent sulphur, and do this at a low cost and without the use of much extraneous fuel. The sintering machine, on the other hand, could take this partially roasted ore mixed with a very small proportion of fine coke or fine anthracite—about 3 per cent—and make an excellent grade of sinter at a high rate—a sinter that could readily be kept down to 0.25 sulphur or less. This sinter required no screening, because there were practically no unsintered fines in it, and even the very small amount of unsintered fines that might occasionally be found would not run over 2 or 3 per cent sulphur, as they had been roasted down to that point during the sintering operation.

The capacity of a sintering machine per square foot of wind-box area when using sulphur as the sintering fuel was usually about one ton per 24 hr., but when using carbon as the sintering fuel, the same machine was capable of handling 2 tons, or even slightly more, per 24 hr. per square foot of wind-box area.

For most plants this was the cheapest form of sintering because every zinc works had large amounts of coke fines available in the form of residue screenings, which were of no value otherwise.

Sintering Machine Only Roasting Device

There is also a third method of sintering zinc ores in which the sintering machine is the only roasting device used. This method was developed in the United States at the California Zinc Co., Winthrop, Calif., and is now used by St. Joseph Lead Co. at Josephtown, Pa. It consists of mixing raw concentrates with crushed sinter low in sulphur, about four parts of sinter to one of concentrates. This charge is sintered, and of the resulting sinter 4/5 is recrushed and returned to the charge, so that every ore particle is passed five times over the sintering machine. The sinter is dense and rather hard fused, just the condition required for use in the electric furnaces used by St. Joseph Lead Co. in its reduction process. This sintered product, however, would be very poor material to put in a retort furnace, because of its dense, fused condition, and if such a sinter were produced in this manner from a western concentrate high in iron it is certain that zinc ferrite would be formed in this repeated sintering.

At the works of the National Smelting Co., Avonmouth, Wales, a sintering procedure very similar to that of the St. Joseph Lead Co. is used. All roasting is done on sintering machines and the charge is made up of crushed sinter and raw concentrates in about the same proportions as used by St. Joseph Lead Co., but only for the purpose of diluting the sulphur of the raw concentrates and rendering the charge porous, so that it can be sintered down to a low enough sulphur content for the retort furnaces. (See p. 418, this volume.) The operation is conducted so as to produce the maximum possible amount of rich SO_2 gas from the concentrates. A relatively thin bed, 3 in. of charge, is carried on the sintering machine and the product is said to be very satisfactory for the retort furnaces, so that evidently it has not the highly fused character of the St. Joseph Lead Co. sinter.

The capacity of sintering machines operated in this way is about 500 lb. of raw concentrates per square foot of wind-box area per 24 hours.

Sintering Flotation Concentrates

Flotation concentrates, because of their fineness, may be quite troublesome in the sintering unless special care is taken in their proper preparation, because without this preparation, they are very apt to cause the formation of a dense bed impermeable to the air, which increases fan power consumption and materially decreases the tonnage output of the sintering machine.

Tri-State district flotation concentrates, Virginia-Tennessee concentrates, and Wisconsin concentrates, all have a tendency to produce beds much more impermeable to the air than have most of the western concentrates. This is largely due to their purity and high zinc contents; because, by the introduction of certain substances or impurities, they can be made to form a very open charge, which passes the air quite freely. Grains of relatively pure zinc sulphide, even when moistened, do not seem to have the tendency to lie apart from one another shown by most lead ores, therefore a bed of such concentrates is lacking in voids for air passages. This deficiency may be remedied by the addition of crushed sinter to the charge, as is done with the return screenings when sulphur is used as the sintering fuel.

Pelleting

It may also be done by pelleting. In pelleting, the moist mass of concentrates is rolled up into many pellets the size of a pea or smaller. To do this successfully it is necessary that the charge being pelleted have certain physical characteristics, and if the constituents of the charge do not have these characteristics naturally, some substance must be added to the charge to give them. This necessary property is the ability of the grains of material to stick together when they are moistened, and hold together when not roughly handled. This pelleting property is almost invariably found in materials containing colloidal matter. For instance, clay possesses it to a great degree. Dry powdered clay mixed with a small amount of water will readily form small balls or pellets that will hold their form in spite of considerable handling, and yet not be wet enough to stick to one another. Pelleted clay can be poured from one container to another and be drawn out of a bin through a gate, handled on a conveyor, etc., almost as readily as jig concentrates would be, and without the pellets adhering to one another.

Residual flotation reagents or oil usually have this property, and often flotation concentrates that otherwise would not form pellets will do so because of an infinitesimally small amount of residual reagents or oil which they contain. Zinc sulphate and iron sulphate, the latter especially, when wet promote the formation of pellets. Practically all oxide fume, fume from baghouses or electrical precipitators, have this property to a great degree, and 1 or 2 per cent of fume added to a concentrate charge will cause it to pellet readily.

The great advantage of pelleting is that it enables the operator to make a charge pervious to air in exactly the degree he desires, out of a material that, because of excessive fineness or some other physical characteristic, such as, for instance, consisting of flat flakes, would cause the formation of a bed highly impervious to air.

The permeability of the bed may be regulated by the size of the pellets. It is possible to mix a charge so as to have it consist of a certain proportion of pellets ⅜ in. in diameter, a proportion ⅛ in., and down to any desired size, which may be as small as 20 mesh. Or it is possible to pellet the charge so that it will consist almost entirely of pellets of 8-mesh size. The size of the pellets and the proportion of large and small pellets to be used will depend on the concentrate to be sintered, and on the depth of bed that it is desired to carry.

Up to a certain size limit, the larger the pellets, the deeper the bed that can be carried on the sintering machine. Practically every zinc works has fine fume of some sort available to mix in with the concentrates to promote pelleting.

Action of Sulphate

The action of sulphate is peculiar. Sulphates in the preroast were the cause of a great deal of woe in sintering plants until it was discovered how to utilize their binding properties. In a charge made up of sulphated preroasted concentrates, where pelleting of the charge is not practiced, the charge after being fed on the pallets will ignite on the top readily enough. The ignition dies out quickly after the pallet passes from under the burner, but if such a charge is poked on the top with a stick halfway down the wind box, it is found to be hard and apparently sintered. However, a peculiar thing is noted: the color does not darken, as ordinarily happens when a charge becomes sintered.

As the pallets pass over the discharge end of the machine, a solid cake can be seen, which breaks off as friable sinter would, but when it is closely examined, it is seen to consist of entirely unsintered material apparently cemented together by some substance. Sintering-plant operators call this material "concrete." It consists of the original preroasted ore grains cemented together by the action of iron and zinc sulphate under the influence of steam generated under the ignition burner. The material is dense, fairly hard, and all pores are imperviously sealed against air by the sulphate acting as a cement. If such a charge is pelleted before sintering, advantage is taken of this cementing property given by the sulphate to hold the individual particles together. Because of the interstices through the bed between the pellets, the air blast has free access, and the ignition flame can be drawn down, thus setting fire to the outside of each pellet on the top surface of the bed.

The sulphides are thus readily ignited, and the bed being permeable air can pass through it and cause sintering to take place through and through. The result is an excellent cake of thoroughly sintered material, because, since there are no excessively large or excessively small ones, all the pellets have a chance to sinter through and through during their passage over the wind boxes. It will be readily understood that a bed composed of substantially round particles, all pretty much the same size, will offer a very even resistance to an air blast over its entire area.

Extremely Fine Concentrates

Of recent years excessively fine zinc flotation concentrates have modified sintering practice, and the indications are that they may bring about still further, rather drastic, changes in procedure.

The flotation concentrates, many of which are of minus 200 mesh, present a serious problem in the preroasting in shelf furnaces, because of the huge amount of dust they make, for one thing, and because of numerous other mechanical difficulties caused by their fineness. This will be referred to further on.

As far as the sintering machine is concerned, the finest flotation concentrates of minus 200 mesh present no difficulties provided they are properly prepared by pelleting. When pelleted, flotation concentrates as a rule yield a product lower in sulphur than would a concentrate of exactly the same chemical composition but whose individual particles were ⅛ in. mesh, and in addition the output in tons of sinter is usually higher than it would be on the ⅛-in. size, because the smaller 200-mesh particles can be desulphurized and sintered more rapidly than the ⅛-in. particles.

Flotation concentrates of the finest character are just as amenable to sintering as other concentrates, therefore, and, as is well known, very little flue dust is made from even the finest of flotation concentrate charges in sintering.

Recovery of Gas for Making Acid

Hence, because of the fact that part of the gases from a sintering machine can be separated from the rest so as to give a product high enough in SO_2 to be utilizable for making H_2SO_4, the possibility of doing all the roasting of zinc sulphides concentrates is receiving consideration generally. Sintering machines have been used for some time in Europe for this purpose—machines specially constructed with a view to trying to get as large a proportion of the SO_2 as possible in the form of rich gas, and at several European works zinc sulphide concentrates are roasted and the gases are utilized for making acid, using only Dwight-Lloyd machines for this purpose. The procedure at the National Smelting Works has already been described.

There is also another method, used by the Overpelt Zinc Works in Belgium, which is peculiar. There the concentrates are preroasted in mechanical roasters down to 7 or 8 per cent sulphur, the roast being conducted so as to produce as much sulphates as possible. If the amount of sulphates is insufficient, the roast ore is moistened with dilute chamber acid to increase them. If necessary, raw concentrates are added to bring up the sulphide sulphur content. The mixture is then moistened and fed into a long steel trough having many drilled holes about 3⁄16 in. in diameter in its bottom. A heavy iron roller runs backward and forward, exerting heavy pressure on the charge constantly being fed into the trough and squeezing this charge through the apertures in the bottom in the form of spaghetti. This is cut off into small pieces and drops on a carrier with a perforated bottom, through which hot air is blown to surface-dry the spaghetti. As soon as this is surface-dry, so that it will not stick together, it is fed to the pallets of a sintering machine in a bed about 10 in. deep. It is then sintered and a very large part of the sulphur is recovered in the form of SO_2 gas, 5 per cent or better, which is sent to the acid plant. The gases from the preroasting furnaces, of course, also go to the acid plant, so that the over-all recovery of sulphur is very high, and only a small portion is discharged into the air as a very weak gas. This comes principally from immediately under the ignition burner and the last few feet at the far end of the wind boxes.

The product is very well roasted, still showing the structure of the spaghetti in the sinter cake. The latter breaks up readily into small pieces suitable for the retort furnace. The great pressure used in forming the spaghetti so compacts the concentrate particles that when the sinter is broken up to ¼-in. pieces, it makes a dense and heavy charge for the retorts, which makes possible a charge of at least 10 per cent more per retort.

In the method in use at Overpelt, the binding action of sulphate is used in a very interesting way, so as to produce a charge of even permeability, which permits the use of a very deep bed in the pallets and therefore the attainment of the conditions under which the gases highest in SO_2 may be obtained, and at the same time to produce a satisfactory sinter. The apparatus for producing the spaghetti is somewhat cumbersome and expensive. Except for the compacting of the charge, pelleting would give equally good results at a lower cost and with much less cumbersome or expensive apparatus. Pellets, if properly made, can be produced so as to make a denser sinter than will a charge made up in the ordinary way without pelleting.

There is absolutely no question that if gases high in SO_2 are wanted, a deep bed made up of a charge that has evenly distributed interstices between spaghetti or pellets of relatively uniform size will give much better results than a comparatively thin bed of material not in pellet or spaghetti form.

Relative Costs

As to the relative costs of preroasting in a shelf roaster and sintering on a sintering machine: it is somewhat difficult to draw exact conclusions because of the great difference in conditions between Europe and America. European zinc concentrates are usually much coarser than American concentrates, a large part of which now run minus 200 mesh. High-class skilled labor is available in Europe at relatively low cost, to conduct fussy operations that require minute care and constant close attention. Health regulations almost everywhere in Europe prohibit the discharging of SO_2 gases into the air, so that often it is not a question of whether it is profitable or not to make the H_2SO_4; it simply must be made at any cost if any operations are to be carried on. A plant roasting and treating a maximum of 25 tons of concentrates per day is called a commercial operation in Europe, and there are a number of works with acid plants that treat no more than this. Some countries give government subsidies, so that sometimes the operation of the plant is profitable only because of the subsidy.

In a European plant where the total tonnage of concentrates to be roasted is 25 tons per day, there is no question that the first cost of installing a plant consisting of one single sintering machine of relatively small size to do all the roasting is lower than the first cost of installing a plant consisting of one shelf furnace and one small sintering machine to do the roasting and sintering, and as a matter of fact, for a company owning a plant having a capacity of only 25 tons per day first cost would be of immense importance. Secondly the cost of operation would undoubtedly be less with the sintering machine only, because the same crew would be required to run the sintering plant whether it was doing the entire roasting or only the finish sintering. Therefore, even with the comparatively coarse European zinc concentrates, the use of a sintering machine to do all the roasting is economically feasible, and may even be decidedly advantageous.

On the American continent, all of our plants have very much larger daily capacities. If a plant were treating concentrates of the same average coarseness as those found in the European plants, whether the plant consisted of shelf furnaces to do the preroasting and sintering machines to do the finishing, or sintering machines only to do all the roasting, would mean very little difference in the labor costs, except that if all the work of roasting were to be done on sintering machines, probably labor of a higher class, and much more skilled, would be required than would be necessary otherwise.

There might be some saving in the first costs of installation, although this would not be at all in the same proportion as with a smaller plant, because to do all of the roasting on sintering machines would require the installation of, roughly, four times as many sintering machines, or machines of at least four times the size. On the other hand, in regard to zinc plants treating the finer concentrates, as is done in most American zinc plants today, some of which run almost exclusively on flotation concentrates finer than 200 mesh, there is quite a different picture.

The fact that the excessively fine flotation concentrates present a serious dust problem when preroasted in shelf furnaces has been mentioned. Furthermore, the costs of upkeep of such shelf furnaces roasting flotation concentrates exclusively is apparently very much higher, and numerous mechanical difficulties occur that do not occur when roasting the coarser concentrates.

It has already been stated that the sintering machine can just as readily treat the finest flotation concentrates as it can coarser materials, and that there is no dust problem to contend with. Also, these fine flotation concentrates are much more readily amenable to treatment by sintering when high in sulphur than would be concentrates of the same analysis but much coarser in grain size. So that when there must be added to the cost of the preroasting plant the cost of expensive dust-settling or precipitating devices, large flues and chambers, etc.—and the increased cost of operation of the shelf furnaces must be taken into consideration—there is a strong probability that it will be found cheaper and more satisfactory to do all the roasting on sintering machines.

DEVELOPMENT IN UNITED STATES

The writer believes that in this country at least, where there is no necessity because of health regulations for catching every last trace of sulphur—and where the sulphur itself has no such high value as to make it financially profitable to catch every last trace—the procedure most likely to prove satisfactory would be one in which a sintering machine or set of sintering machines would treat a charge composed of two parts of crushed sinter and one part of raw concentrates, this charge having a sulphur content of 12 to 14 per cent and this machine or machines to be run with a view to producing the gas most suitable for the acid plant, without making any attempt to get the sulphurs in the sinter down to the low limit or paying much attention to the physical character of the product.

There would then be another machine or set of sintering machines to which this poorly sintered product, still carrying perhaps 2 to 3 per cent sulphur, would be sent, to be crushed if necessary and mixed with a suitable amount of carbon fuel and sintered; the machines to be operated without any attempt to recover the small amount of sulphur still left in the material being sintered, and run solely with a view to getting a very low sulphur product and a perfectly sintered one.

A procedure of this sort undoubtedly will be more profitable from a financial standpoint and better adapted to American requirements than would be a copy of the European procedure. In the proposed procedure, the first set of sintering machines would be run solely with a view to obtaining the highest efficiency in making suitable gas for the acid plant; the second set solely with a view to making good sinter; whereas the European procedure is a compromise in an attempt to make good gas and good sinter at the same time—and the operating conditions for making good gas are not those required for making good sinter.

There is one sintering plant in this country using gases for making acid, that of the National Zinc Co. at Bartlesville, Okla. No information is available as to operating results. Both shelf furnaces and sintering machines are used.

Production of Cadmium

One recent and very interesting development is the production of cadmium from zinc concentrates. Nearly all zinc concentrates contain small percentages of cadmium. It has been known for a long time that this cadmium could be partly driven off in sintering provided the temperatures of the reaction were high enough, and at many of the earlier zinc-sintering plants an initiated person could tell from a mile away whether or not the sintering plant was making good sinter, by observing the color of the smoke coming out of the stack. If this smoke was barely visible, or very light bluish, the sintering plant was doing poor work. If the smoke was dense, with a pronounced yellowish brown tinge caused by cadmium compounds, the sintering plant was doing first-class work.

This was simple because when the temperatures developed in the bed were high enough to produce good sinter, they also were high enough to drive off considerable amounts of cadmium.

At first there was no particular enthusiasm shown over this, because the driven-off cadmium was lost. When it remained in the sintered product, it was partly recovered in the zinc retorts, and was sold as zinc.

In some zinc works, by special attention to the sintering and elimination of cadmium, a grade of zinc could be produced from the sintered product that could be sold as brass special. Usually this was the metal from the first draw, or the first and second draws.

By operating at a high sintering temperature, zinc concentrates that contained lead but practically no silica could also be caused to lose some of this lead by volatilization. However, this loss of lead, like the loss of cadmium, was usually of no advantage, as lead also if left in the sinter would eventually find its way into the Prime Western grade of zinc, where it would have the same market value as the zinc itself.

Hence there was no advantage usually in driving these metals off, but actually a disadvantage, as they were not recovered, most zinc works having neither baghouses nor Cottrell precipitators.

While cadmium could be partly driven off in sintering, it could usually not be completely driven off, because cadmium driven off in the upper part of the sinter bed would be condensed and deposited in the lower part of the bed, which was still comparatively cool. When the cake was sintered down to the grate bars, there would still be considerable cadmium to be found as a yellow deposit on the metal of the grate bars, in the grate-bar slots, on the pallet sides, and even on the bottom of the cake itself. As the cake was discharged off the sintering machine, much of the cadmium deposit on the bars was dislodged and went down the chute with the sinter, so that a clean elimination of cadmium was never possible.

Several patents had been taken out which contemplated splitting the sinter cake into two or more layers—one rich in cadmium and the others low—but as even these did not make a complete separation of cadmium from any portion of the sinter, they found little practical application. If cadmium and lead could be completely volatilized in sintering, a pure zinc could be made in the retort furnaces from ordinary western ores, but otherwise there was no particular advantage in fostering the partial volatilization of the cadmium.

In the last year, however, there has been a decided change, brought about in part by the use of cadmium for electroplating but principally by the use of cadmium in bearing metals for automobiles. The demand so created has resulted in an increase in the price of cadmium metal to about twice its former price, with the result of making it highly profitable for a zinc works to drive off all the cadmium possible from its ores and recover it as a by-product.

The action of sodium chloride in roasting to promote the formation of easily volatilizable chlorides has been known and used for years on copper and other ores. It was found that the addition of salt in small proportions—about 10 lb. per ton—to a sintering charge, and the close observation of certain operating conditions would make it possible to eliminate the cadmium, all of the lead, and all of the residual sulphur from ordinary ore, so that a sinter carrying 0.000 per cent cadmium, 0.000 per cent lead and 0.000 per cent sulphur could be produced. With such a sinter, zinc metal running 99.99 per cent zinc could be produced in ordinary retort furnaces—and, still more important, nearly all of the cadmium and lead could be caught by a Cottrell apparatus. With cadmium metal selling at $1.05 a pound, there was a very great inducement to remove cadmium from the ores.

With a zinc concentrate carrying only 0.3 per cent cadmium, the value of the cadmium contents as refined metal would be about $6. It is not astonishing, therefore to find many zinc works in that past year and a half increasing their plant capacities or changing their methods of sintering so as to recover as much cadmium as possible. This will probably result in a decrease in the tonnage of Prime Western grade of zinc produced and an increase in production in zinc metal of higher grades.

The Warner-Ingalls Zinc-roasting Process

By Munroe F. Warner,* Member A.I.M.E.

As originally built, the plant of the American Zinc and Chemical Co. at Langeloth, Pennsylvania, was based upon the Joplin and Wisconsin fields as primary sources of zinc ores, the ores being the then normal jig and table concentrates. Construction incorporated standard Matthiessen and Hegeler kilns without regenerators.

With the development of differential flotation, zinc concentrates produced by that process became the basis of operation. These concentrates were very fine, upwards of 90 per cent passing a 300-mesh screen, and had a comparatively low fusing point with marked caking and crusting characteristics.

Difficulties and losses quickly developed. In roasting, the ore went through a decidedly fluid state, and spills became serious. Caking and crusting on hearths was severe and dust losses throughout became intolerable. Acid recoveries dropped from the normal ton-for-ton level to 0.85 tons per ton of ore, and choking of Glover towers and acid lines became a problem.

In 1926 and 1927 a two-unit sintering plant was built and placed in operation in accordance with the Baelen process for finishing desulphurization with admixture of carbon. This had its beneficial effect in smelting, but the other problems remained.

The problem presented was the roasting of Pecos flotation concentrates at the rate of 200 tons daily to a sulphur content suitable for finishing in the sintering plant. Specifications had to be governed by the existing acid plant of four chamber sets built in units of two, rather widely separated, and the sintering plant built in the space between the existing pairs of kilns, of which there was one on the center line of each of the four chamber sets.

The problem contained elements of pioneering and experimentation. A thermal analysis and heat balance clearly demonstrated a possibility of accomplishing autogenous roasting, well worth the attempt, because of high fuel costs and resultant economies in operation of the acid plant due to decreased gas volumes and a consequent release of capacity for increasing acid production, a problem also faced.

Manuscript received at the office of the Institute June 18, 1936; revised Aug. 31, 1936.

* Consulting Metallurgist and Chemical Engineer, Newark, N. J.

The only roasters in existence designed to accomplish an autogenous roast were the Ore Roasting Development Co. roasters of Fogh in operation at the Columbus plant of the American Zinc Oxide Co. While these were built with muffles under the two lower hearths as a reserve, the roasters were operated at times autogenously and the muffles were blocked off and considered a disadvantage by the operator and responsible for the necessity of using a small amount of direct-fired gas. The Fogh principle of division of the ore and multiple feeding, resulting in by-passing certain hearths, is reflected in the design adopted.

Available information relative to roasting elsewhere was studied, particularly practice at Columbus, in England and Belgium with the Spirlet roasters, and in Australia and Africa with Skinner and Herreshoff roasters. In this the cooperation of Thomas A. Dickson, of the Colorado Iron Works Co., and the late Leslie H. Webb is acknowledged.

Late in 1927 a decision had to be made and, following inspection of the new 12-hearth Herreshoff roasters operating at Bartlesville as pre-roasters in Rigg's sintering process, of the six-hearth Skinner roaster at Rifle, Colo., and such consideration as time permitted of Coolbaugh's down-draft process modified to produce oxide instead of sulphate by the addition of sulphide at the end of the roast in accord with the classic reaction $3ZnSO_4 + ZnS = 4ZnO + 4SO_2$, it was decided to build four roasters to specifications to be drawn by Walter R. Ingalls, consulting engineer for the company, and the author. These specifications may be summarized as follows:

SPECIFICATIONS FOR ROASTERS

The objective being autogenous roasting, heat conservation and thermal stability had to be carefully considered. To this end certain of the specifications were drawn, and experience with this ore on the Hegeler kilns dictated others.

The roasters were specified to be 20 ft. inside diameter, of 12 hearths, and with effective hearth area of 3400 sq. ft. each, based on a factor of sulphur elimination of 10 lb. per square foot. The actual figure for 60 tons of 30 per cent ore roasted to 3 per cent sulphur was 3275 sq. ft.

The walls were specified 18 in. thick, 9 in. firebrick, 4½ in. insulating brick and 4½ in. common red brick for the lower third and 9 in. each of firebrick and red brick for the upper two-thirds.

The hearths were specified to be flat and horizontal, as a result of experience with this ore in the Hegeler kilns with respect to the fluid phase through which it goes, and of solid tile without horizontal joints because of trouble experienced with such construction in those kilns. Filler tiles, used to make a flat hearth surface, pull out as a result of crust formation which necessitates abnormal chiseling.

The shell specification is not unusual except that heavy inside bands were specified, to assure support of the hearths vertically and take the load off the side walls. The hearth skewbacks were molded to fit over these bands at the thrust line.

Aside from the design permitting deep arm sockets for the support of the long arms necessary, the feature of the central shaft and assembly specification is that cooling air circulation is the reverse of normal, the air entering the top of the shaft and discharging at the bottom. The maximum cooling effect was desired in the upper part of the roaster, with less effect at the bottom, hence the specification. Lagging of the shaft with 4½ in. of firebrick was specified for greater thermal stability and as protection against corrosion.

In order to utilize the heat in the cooling air discharged at the bottom of the central shaft, means of piping the air therefrom and conducting it for admission into each of the four lower hearths, and under valve control, was specified, air piping to be insulated. This was later changed to extend distribution throughout the roaster by means of two diametrically opposite risers, each admission port being valve-controlled, and the risers ending in bleeder valves for controlling total process air and wasting the excess.

A stack for creating draft to maintain circulation of cooling air in the reverse direction, with the necessary dampers to effect this, was specified to be mounted on top of the central shaft for use if the forced-draft cooling should fail.

Since the ore was to be delivered with 3 to 4 per cent moisture, drying for dependable feeding had to be completed at the roaster. The top hearth was specified to be thin and conical, and four rabbling arms were specified, to be tapped into the hot-air passages of the central shaft and equipped to discharge heated air under damper control over the ore on that hearth.

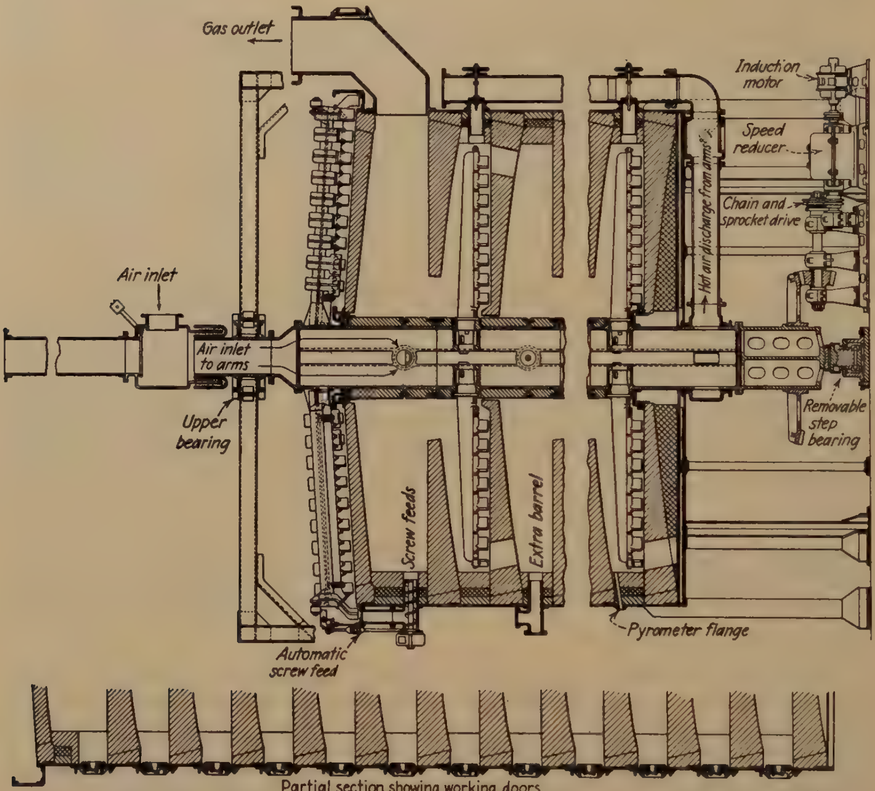
Means of subdividing the ore and feeding it at several points were specified, partitioning to be by means of an annular trough surrounding the drying hearth, and from there by vertical drop pipes to the four feeders on No. 1 hearth and two each on Nos. 3, 5 and 9.

Specifications were also made covering extra sockets in the central shaft for plain arms for additional cooling on hearths 2 to 5, with the arms included. This idea was later abandoned because of complications in central shaft design resulting in restriction of cooling-air passages.

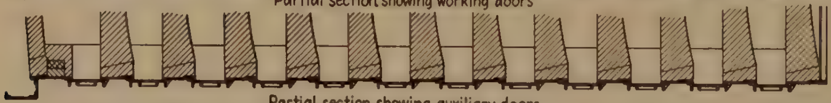
Consideration was also given to the use of four arms on the bottom hearth, but this was rejected in preference to use of a greater number of smaller rabbles to accomplish the same result if found necessary.

Rabbles were specified of alloy, and arms partly alloy and partly cast iron. Later this was modified to include noncooled alloy arms for the lower three hearths instead of normal air-cooled arms.

Mechanical specifications were left to be worked out in design, except that a preference for a tapered roller type of step bearing for the central shaft was expressed.



Partial section showing working doors



Partial section showing auxiliary doors

FIG. 1.—GENERAL SECTION, BETHLEHEM-WEDGE ROASTER INCORPORATING WARNER-INGALLS SPECIFICATIONS.

The general purpose of these specifications will be observed to effect flexibility in ore and air distribution, both under control.

INSTALLATION

The contract for four roasters was let early in January 1928 to Bethlehem Foundry and Machine Co., and design under the author's direction was started immediately. To meet the specifications, this was original with the exception of the unique cruciform section accepted and used in the design of the central shaft, and such standard parts as arms and rabbles, doors and frames, etc., modified as required.

The design in accordance with which the roasters were built is shown in Fig. 1. The cooling-air circuit with admission into the top of the central shaft, the means of distributing the heated air to the several hearths and controlling it, and the method of emergency cooling of metal parts by reversing the direction of air flow, are all evident.

The ore is fed at the inside of the drier hearth and rabbled outwardly into the annular trough around the periphery of the hearth, around which it is carried by pushers on the ends of two of the rabble arms and from which it feeds vertically downward through the drop pipes shown. The ore is fed into the roaster by means of screw feeders, which were operated through an adjustable throw tripping mechanism by the drier hearth arms. This method was unsuccessful, imparting a violent shock, which jarred the entire roaster, and was replaced by individual motors driving through speed reducers and sprocket and chain, rate of feed being changed by substituting drive sprockets of the desired size, the feeders then running continuously.

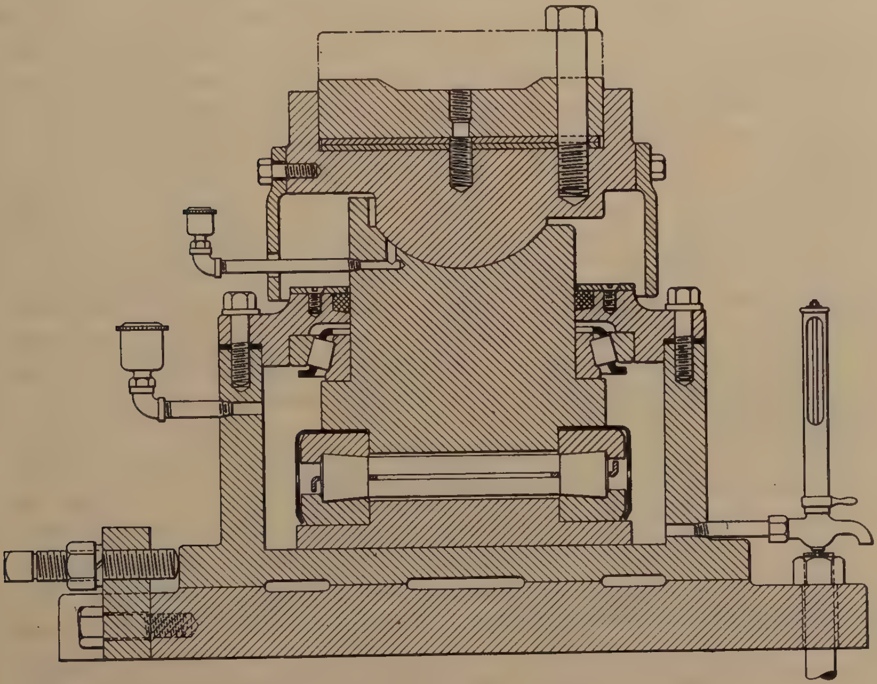


Fig. 2.—Step bearing assembly.

The utilization of preheated air discharged on the drier hearth will be observed. Each of these arms has a butterfly valve to control the volume of air used. Because of dusting due to effective drying, several of the outside nozzles of the air pipe were plugged and the heated air discharged from approximately two-thirds of the arm length on the trailing side at an angle about 35° downward from the horizontal.

The cruciform design of the central shaft permits a deep arm socket without too much restriction of the air passages. The hot-air pass is central. The central shaft is mounted on a ball-and-socket bearing incorporating a Timken tapered roller step bearing (Fig. 2) rated at 265,000 lb at 2 r.p.m. As originally designed the ball and socket had a radius of 12 in., and the bearing failed, the roller retainers of soft steel wearing out rapidly and the rollers grinding to breakage. The ball and socket was redesigned with a radius of 4½ in., and the roller retainers were hardened by carburizing, no failures having occurred with these. The bearing is adjustable vertically by means of shim plates and may be removed and replaced as a unit by jacking up the central shaft an inch or two.

The drive is by means of a 15-hp. constant-speed motor, gear reducer, roller chain and sprockets, and bevel pinion and ring gear. Changes in speed are accomplished by changing the driven sprocket. Changes in speed of both the ore feeders and the roaster itself are effected by changing sprockets in the drives. This was done so that a setting made would be inflexible until changed by order of the proper authority, and prevented variable operation, which would have ensued had variable-speed drives been used.

Gases leave the roaster from a single outlet at the top hearth, and ore is discharged from a single drop hole in the bottom hearth. Originally, because of a requirement that the ore be weighed, the ore was discharged through an air-lock type hopper into closed cone-shaped tramcars, weighed and discharged into an elevator and bin serving a Baker ore cooler delivering to the sintering plant. Because of the dust, mechanical handling was necessary. The conveyors selected were ordinary cast-iron screws in cast-iron troughs, the screws being 16 by 16 in., to handle chisel lumps and operating at slow speed. These served an elevator specially designed for the prevailing temperature, which discharged into a similar screw conveyor delivering to the roasted-ore bin. In early 1934 this conveyor system had operated five years without major replacements because of wear, and handled the chisel lumps with very infrequent choke-ups.

With the exception of the drier hearths (Fig. 1), in which there are two removable tiles for emergency ore-feeding, hearth design is shown in detail in Fig. 3, and accords with specifications. The tiles are thin enough in one dimension to insure sound manufacture and thorough burning, and all refractories, excepting side-wall lining, were set in chrome cement made by mixing furnace chrome and sodium silicate, only necessary chipping and hand-stoning for a reasonable fit being done.

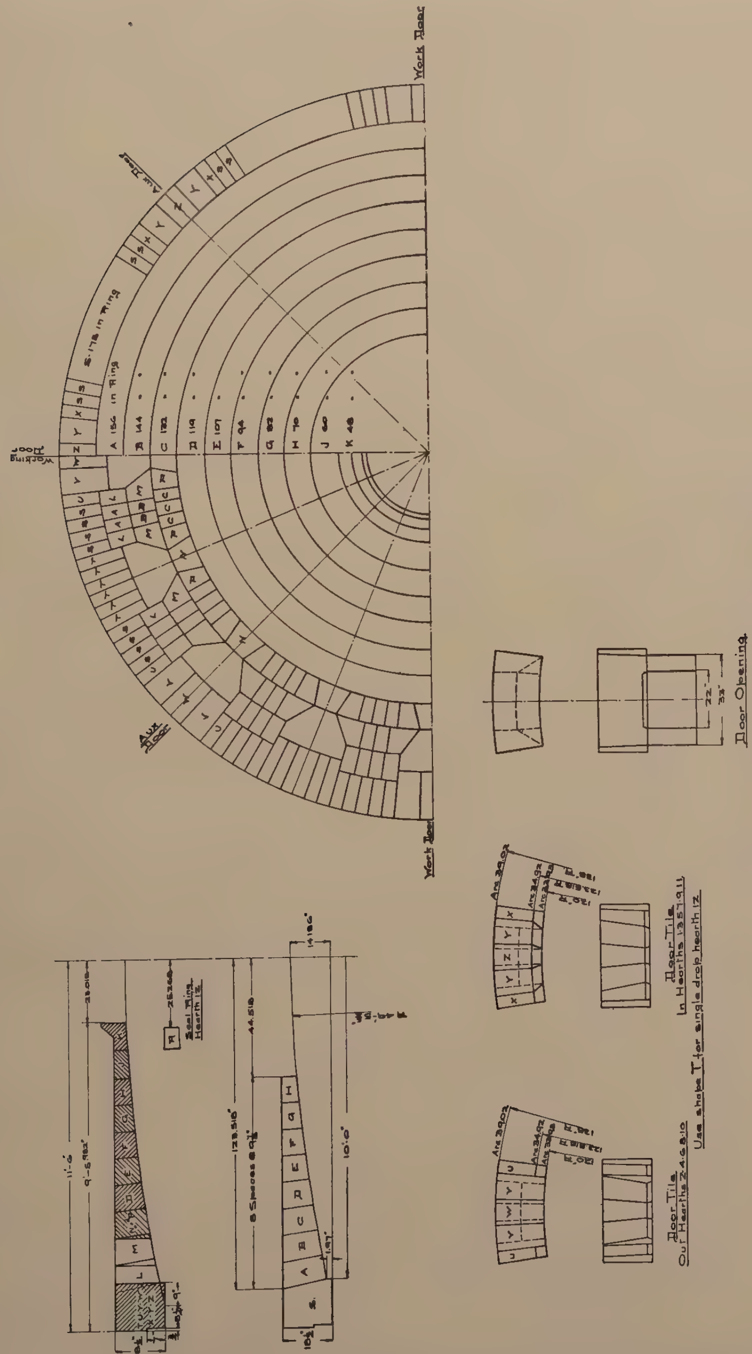


FIG. 3.—WARNER-INGALLS HEARTH DESIGN.

The refractory was a Walsh (Missouri) mix analyzing: SiO_2, 55 per cent; Al_2O_3, 42; Fe_2O_3, 1.8; CaO, 0.3; MgO, 0.3, alkali, 0.7. This was specified as being more stable in expansion and shrinkage under the temperatures of the operation, and more corrosion resistant than the higher silica refractories normal in the industry.

Drop holes number 16 per hearth at 2 sq. ft. each, with the inside drop of equivalent area, the design being based upon conserving the maximum hearth area for hearth roasting.

Positive seals were not provided except the alloy-iron seals on the drier and bottom hearths, it being felt that minimum clearance around the central column would not result in sufficient short-circuiting of gases to be of moment. This was borne out in practice.

Rabble arms were of a design on hand, of round cross section with horizontal diaphragm, with noncooled arms of the same design without diaphragm and open on the bottom between the rabble rails. Both cast-iron and chrome-iron arms were specified, both of the same dimensions and same wall thickness, one of the two reasons for using chrome iron being greater strength, weight for weight, the other being greater resistance to corrosion. As equipped, one roaster had a cast-iron arm and an alloy arm on the upper nine hearths. In general, however, cast-iron arms were used on No. 1 (the top) hearth, alloy arms on Nos. 2, 3, 4, and 5 hearths, cast-iron arms on Nos. 6, 7, 8 and 9 hearths, and noncooled alloy arms on Nos. 10, 11 and 12 hearths. Rabbles were all of chrome iron, with a set of cast-iron rabbles as spares. The latter, however, wore very rapidly, oxidized badly, and tended to break off and damage following equipment.

The noncooled arms did not prove entirely satisfactory, tending to warp and twist, particularly whenever it was necessary to use auxiliary gas-firing to regain lost temperature. Standard alloy arms with air ports blocked were satisfactory, but finally it developed that standard air-cooled cast-iron arms could be used in the bottom hearths without measurable loss of heat, and noncooled arms were abandoned.

Air-admission arms—i.e., arms with holes in the bottom face to discharge air directly on the hearth—were tried and rejected, because reversal by stack draft when used in chiseling drew gases and dust into the cooling circuit and threatened trouble.

Observation of the spreading of oxidizing air over the hearths from the air ports plainly showed adherence to hydraulic principles, the air admitted at lower temperature than the hearth temperatures being as effective as air injected through arm nozzles.

Original arms proved too small in section and resulted in creation of high back pressures, shortage of cooling air and high air temperatures. Larger arms of the diaphragm type were designed and proved more successful. A later design, incorporating a central tube instead of the diaphragm, was tried and found to have greater warping deficiencies than the diaphragm type. The arm design finally evolved was of the diaphragm type, and square in section, to allow a maximum air-pass area within space limitations, and also to improve the strength and resistance to warping.

With an arm properly designed from experience, the problem is one of manufacture to attain uniform thickness of walls. Otherwise warping results and an expensive arm, without salvage value, is lost. A dependable arm in this respect would justify the use of alloy throughout, such an arm having almost unlimited life. Cast-iron arms are much more fragile; they should be operated at lower temperature with more cooling air; they oxidize and corrode rapidly in the high-sulphur zones and freeze valuable rabbles, which may thereby be lost. The preferred arm assembly for this roaster is air-cooled alloy for the upper nine hearths, and air-cooled cast iron for the lower three hearths. The alloy specifications used were the following:

Cr.	26	and	28 to 30
Ni.	2 max.		2 max.
Mn.	0.12 to 0.20		0.12 to 0.20
Si.	0.50 to 0.70		0.50 to 0.70
C.	0.60		0.60 to 0.75

The higher chromium-carbon specification is preferred. Difficulties and complications in machining higher carbon-chromium irons limit the carbon specification to about 0.75, otherwise this specification would preferably be 0.90 to 1.00 and might be raised as high as 1.50.

Original rabbles were of standard Wedge design, having blades 12 by 6 by 1 in.; were spaced 9 in. and integrally cast with holder to slide on the rabble rail on the bottom of the arm. Later the rabbles were redesigned to increase the rabbling effect. The reduction in size of rabble effected improvement in results with respect to sulphur in the roast, sulphide sulphurs being lower or sulphates higher. Alloy specifications in order of time are given in Table 1.

TABLE 1.—*Alloy Specifications for Rabbles*

Cr.	26 to 28	26 to 28	27 to 30	26 to 30
Ni.	2 max.	2 max.	2 max.	0.5 max.
C.	0.60 to 0.75	0.50 to 0.70	0.40 to 0.50	0.60 to 0.75
Mn.	0.12 to 0.20	0.12 to 0.20	0.10 to 0.20	0.12 to 0.20
Si.	0.50 to 0.70	0.60 to 0.70	0.40 to 0.50	0.50 to 0.70

With the exception of the 0.40 to 0.50 C specification, which bent under the load in the hotter hearths, there was little choice in any of these specifications, they being in fact very similar.

Breakage did not occur, even under severe heat shock of the chiseling operation, wear due to abrasion was not severe, and indicated that the minimum life was nine months to a year in the hottest zones, where the sulphur content is still high. The most severe conditions in this respect occurred on hearths 2 and 3, and the severity of corrosion was very definitely a function of the lead content, probably sulphide in nascent stages of oxidation. The Pecos ore, upon which the operation was based, contained 1.50 to 1.70 per cent Pb. In treating another ore, which contained from 2.15 to 2.78 Pb, the corrosion was much more rapid and rabble life decreased to six months or less.

Corrosion

Results of a test indicate the character of rabble corrosion, a test in which a number of rabbles supplied by the Duraloy Company were assembled to determine corrosion-resistant qualities at several points. Analyses of the alloys are given in Table 2.

Table 2.—*Analyses of Alloys*

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Cr......	28 to 30	28–30	32–35	32–35	28–30	27–30	26–28
Ni (max)	0.50	0.50	0.50	0.50	0.50	2.00	2.00
Si.......	0.50–0.70	0.50–0.70	0.50–0.70	0.50–0.70	0.50–0.70	0.40–0.50	0.50–0.70
Mn (max).	0.50	0.50	0.50	0.50	0.50	0.10–0.20	0.12–0.20
C.......	1.5–2.0	1.5–2.0	2.0–2.5	2.0–2.5	0.20–0.30	0.40–0.50	0.60–0.70
Ti.......	0	2–3	0	2–3	1.40–1.60		

The rabbles were scattered through the upper 10 hearths in predetermined order to cover all conditions.

After service test of six months, the rabbles were removed and examined. Corrosion was hardly noticeable on No. 1 hearth, was evident and distinct on Nos. 2 and 3 hearths, much less evident on No. 5 hearth, and practically lacking below that hearth. Location of the rabble radially had no observable effect on corrosion.

Corrosion on the rabble face was characteristically evidenced by scoring in the form of one or more grooves coinciding with the wash contour, and above that, by honeycombing and hard adherent scale in the zone of high temperature and high sulphur, hearths 2 and 3, where corrosive compounds are forming and occur in progressive states from nascent to products released from the bed as vapor, fume and gas. Face wastage is due to combined mechanical abrasion and corrosion, being decidedly less below the wash line. Wastage on trailing surfaces is primarily corrosion, these surfaces being fully exposed and corrosive vapors being concentrated there by the rotation of the assembly.

It is concluded from this that chromium content should be not less than 28 per cent, 32 per cent being preferable on the hearths where fuming occurs; that carbon should be not less than 1.5 to 2 per cent with 2 to 2.5 per cent range preferred; and that titanium appears to improve the corrosion resistance where that effect is severe.

Dust Collection

The flue system, containing the dust collector and draft fan, was of unlined steel plate and extended from the roaster to the existing brick flue of the respective acid set. The average new flue was approximately 30 ft. from roaster to fan, with the collector equidistant from each.

Dust collectors were the then newly developed American Blower Company's Sirocco, the size used being D-30 for 15,000 cu. ft. per min. of gas at 1000° F., with a pressure drop of 1½ to 2 in. water. These were placed close to the roasters, one for each roaster, and discharged through a double gate into a screw conveyor, to return the dust continuously to No. 7 hearth of the roaster.

The draft fans furnished by the Robinson Ventilator Co. were of equivalent capacity, of Sirocco impeller type, with double inlet and central impeller, and were built entirely of chrome iron without water cooling except for the sleeve bearing oil reservoirs. They were driven by variable-speed 10-hp. motors to control the pressure at the roaster-gas offtake at zero.

While two installations of these collectors on pyrites burners had operated satisfactorily, there had been none for the particular conditions to be met, and some troubles in addition to opening of seams and leakage were experienced in operation.

Granular dust was almost completely removed, but oxides carried through to convert into sulphated fume and deposited throughout the entire system up to dust chambers at the Glover towers, requiring considerable cleaning of flues.

With high-lead ores, 2 to 3 per cent Pb, the fume built up in rocklike character and could be removed only by manual chiseling, the critical temperature being that at the dust collector and a few feet beyond.

Fume deposits on the fan impeller resulted in unbalance and vibration, and was largely rectified by impellers of the paddle-wheel type, which are more easily cleaned, by an increase in shaft diameter and substitution of Timken bearings with oil-circulating system for the original sleeve bearings.

Conclusions drawn from experience with this system indicate that a brick-lined collector would have been preferable, placed as close to the roaster as possible, to the extent of making it the gas offtake, thus removing the maximum of ore dust and oxide before it could be converted into fume by reaction with the gas and a lowered temperature. The draft fan should then be placed as close to the collector as possible and connected by an insulated and lined flue for maintenance of temperature.

Since fume formation is a function of the temperature, and sulphated fume settles out readily, temperature may be used as a guide to selection of dust chamber versus Cottrell, as dictated by heat requirements of the Glover tower and by brimstone provisions, any sulphated fume carried beyond the sulphur burner connection being subject to thermal dissociation into oxide and thus carried into the Glover tower.

OTHER EQUIPMENT

Pyrometric equipment consisted of Chromel-Alumel couples on each hearth (Fig. 1), and a couple at the hot fan, all connected to an indicating pyrometer through a multiple-point switch.

All control switches, regulators, thermometers, pyrometers, instruments and gauges were brought to a common control panel for two roasters, located on the top floor. Auxiliary controls and certain other controls were placed at convenient points.

An exception to normal practice was in making the top floor—even with the drying hearth—the operating floor. This is permissible because the ore contains sufficient moisture to eliminate the dust nuisance, and the roaster draft is under fan control to eliminate normal gas nuisance. With ore feeders and much equipment at the top elevation, that was determined upon as the point of operating control, making possible a closely regulated flow of ore, observation of the operation of the roaster feeders, and proper care of the draft fan.

Inasmuch as the ore was to be dried to only 3 to 4 per cent moisture to reduce or eliminate dust losses, and the tendency to pack and hang up had to be met, a plan had to be worked out for handling the green ore. Drying, screening and crushing equipment, in a building some 400 ft. distant and at a much lower elevation, was completely revised and replaced to deliver dried ore to feeder bins there, subject to roaster demand. The conveyor system comprised pan feeders under these bins delivering to some 500 ft. of belt conveyor with two transfers, equipped with an automatic scale and a lifting magnet, and discharging finally onto a shuttle conveyor for delivery to any one of four 80-ton capacity bins, one for each roaster. The conveying system was designed to deliver the requisite tonnage within three to four hours at full demand. Control is carried to a central point at the discharge onto the shuttle conveyor, and the entire transfer system from the dry-ore bins to the roaster bins is operated from this point by one man in 2 to 3 hr. per day.

The roaster bins are suspended from the building structure, the bottoms being closed. Feeders are heavy screws, 16 by 16 in., working across the width of the bin within the ore, and discharge onto belt conveyors delivering to the respective roasters. The feeders are driven by a 3-hp. variable-speed motor through a speed reducer and gears by a train of intermeshed gears in tandem, one for each screw.

To overcome difficulties due to packing of the ore around the screws, it became necessary to add a lattice over the screws, the final lattice completely covering the screws with the exception of a slot 7 in. wide the full length of the screws over the space between adjacent screws where the thrust reaction of the flights has an upward component. As thus modified, the feeding of the moist ore was successful.

As built then, the roasters are in units of two each, one unit on each side of the sintering plant, and each unit delivering ore through a mechanical handling system and a Baker ore cooler to one of the two units of the sintering plant. The ore is handled mechanically throughout and the layout is arranged so that two ores can be worked at one time.

Some quantities required per roaster were:

Iron castings	144,700 lb.	Red bricks	10,500
Steel plate	82,800 lb.	Firebricks	12,500
Structural steel	14,700 lb.	Insulating bricks (4 hearths)	2,000
One rabble arm	1,000 lb.	Tile	435 tons
One arm dressing	300 lb.		

Acknowledgment is here made of the services of the writer's assistant, R. E. Clark, in supervising the contractor's structural design, inspecting erection, directing installation of machinery and equipment, and in being of material assistance throughout. Commendation is due the operating staff and personnel under D. C. Wray, superintendent, for maintaining production without serious interruption during construction of such magnitude in the midst of operations.

METALLURGICAL OPERATION

The first roaster, No. 3, was completed early in November 1928, and immediately placed in operation while construction was still going on.

The roaster was preheated with natural gas to as high a temperature as possible and the ore was started. Very shortly temperatures came up but the operation was thermally unstable at initial low tonnage. Speed was reduced from 1.5 r.p.m. to 1.25 and 1.0 with improving results, and from then on only those troubles normal to a new operation were experienced, principally with the mechanical feeders and the central column bearing, as previously described.

The roaster speed at the start was 1.5 r.p.m. At this speed the ore bed was thin and the roaster sensitive to heat changes. The speed finally adopted ranged from 0.75 to 1 r.p.m. with resultant heavier bed and a greater heat stability. Replacement of the original trip mechanism driving the screw feeders, by individual motors operating continuously, solved that problem and effected dependable operation and hoped-for results.

Tonnages ranging from 42 to 62 were, in normal practice, roasted successfully without using extraneous fuel. Tonnages under 42 resulted

TABLE 3.—*Typical Roaster Log, American Zinc & Chemical Co., Langeloth, Pa.*
Dec. 1, 1933

Time	6 A. M.	7:30	9:00	10:30	12N	1:30	3:00	4:30	6:00	7:30	9:00	10:30	12M	1:30	3:00	4:30	Feed	Air	Ore Pecos
			Chiseling		Chiseling														
Roaster No. 3																			
Temperature, deg. F.																			
1	1180	Cleaning flue	1160	1180	1160	1130	1160	1160	1160	1160	1160	1160	1160	1160	1160	1160	2	Dr 4	Scales—reading
2	1470		1450	1440	1440	1410	1440	1440	1440	1430	1430	1430	1430	1430	1430	1430		Bl 0	Start
3	1320		1320	1310	1310	1300	1300	1300	1300	1300	1290	1300	1300	1300	1300	1290	1		Finish
4	1410		1410	1400	1410	1400	1400	1400	1400	1400	1400	1390	1390	1390	1390	1380		6 turns	Green ore, lb.
5	1300		1290	1280	1280	1280	1280	1280	1280	1280	1270	1260	1270	1270	1270	1270	1		Moisture, per cent
6	1340		1330	1310	1330	1320	1330	1320	1330	1320	1320	1320	1320	1320	1320	1320		11	Dry ore, 51.5 tons
7	1320		1310	1300	1310	1310	1310	1310	1310	1310	1310	1300	1300	1300	1300	1300			Flue dust, lb.
8	1340		1330	1320	1330	1330	1340	1340	1340	1330	1330	1320	1330	1320	1320	1330		11	Fuel
9	1320		1310	1300	1310	1300	1300	1310	1310	1300	1300	1300	1300	1300	1300	1300			
10	1350		1340	1320	1330	1340	1340	1350	1340	1340	1340	1340	1340	1340	1340	1340		11	
11	1380		1370	1350	1360	1360	1360	1370	1360	1360	1370	1370	1370	1370	1370	1370			T.S. 2.55 St 1.17 Sd 1.38
12	990		970	950	950	950	960	970	960	960	960	960	960	960	960	960		4″	Sint. S—on S—off
Fan	790		790	770	780	750	770	790	800	790	790	780	780	780	770	780			
Air	370		360	360	360	360	360	360	360	360	350	340	340	350	350	350			
Pressure, H_2O																	Chiseled Nos. 2-1 hearths.		
Air	4.7		4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.7	4.4	4.4	4.	4.	4.	4.	Remarks: Cleaned outlet. Chiseled the		
Flue	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	dry pan.		
Fan	3.		3.	3.2	3.	3.	3.1	3.3	3.3	3.3	3.	3.	2.9	2.9	2.9	2.8			
Gas																			
SO^2								6.			6.			6.2		6.2			
O								8.4			8.6			8.4		8.4			

Time	6 A. M.	7:30	9:00	10:30	12N	1:30	3:00	4:30	6:00	7:30	9:00	10:30	12M	1:30	3:00	4:30	Feed	Air	Ore Pecos
				Chiseling															
Roaster No. 4																			
Temperature, deg. F.		Cleaning flue																	
1	1340		1300	1320	1310	1310	1310	1320	1320	1320	1320	1320	1320	1320	1320	1320	2	Dr 4	Scales—reading
2	1440		1420	1420	1420	1420	1420	1420	1430	1420	1430	1420	1430	1430	1430	1430		Bl 0	Start
3	1290		1280	1280	1280	1280	1280	1280	1280	1280	1280	1280	1280	1280	1280	1280	1		Finish
4	1430		1420	1420	1420	1420	1420	1420	1420	1420	1420	1420	1420	1420	1420	1410		3 turns	Green ore, lb.
5	1370		1360	1360	1360	1360	1360	1360	1370	1370	1370	1370	1360	1360	1360	1360	1		Moisture, per cent
6	1410		1400	1400	1410	1410	1400	1410	1410	1410	1410	1410	1400	1400	1400	1400		12	Dry ore, 51.5 tons
7	1420		1410	1420	1410	1410	1410	1410	1420	1420	1420	1420	1410	1410	1410	1400			Flue dust, lb.
8	1330		1330	1340	1320	1330	1320	1330	1330	1330	1330	1340	1330	1320	1320	1320		12	Fuel
9	1340		1330	1340	1310	1320	1320	1340	1340	1340	1340	1340	1330	1330	1330	1320			
10	1360		1340	1360	1340	1360	1360	1360	1370	1360	1360	1360	1360	1360	1360	1350		12	
11	1320		1300	1310	1310	1310	1310	1320	1320	1320	1320	1310	1310	1310	1310	1300			T.S. 2.40 St 2.37 Sd 0.03
12	1060		1060	1090	1090	1070	1100	1120	1100	1080	1060	1050	1050	1050	1050	1040		4″	Sint. S—on 3.07 S—off 0.05
Fan	740		650	690	680	680	680	690	690	690	690	680	690	690	690	690			
Air	410		420	420	420	420	420	420	420	420	410	400	400	400	400	390			
Pressure, H_2O																			
Air	5.2		5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2			
Flue	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00			
Fan	1.6		1.6	1.8	1.9	1.9	2.	2.	2.		2.	2.	2.1	2.1	2.1	2.1			
Gas																			
SO^2								6.			6.			6.2		6.2			
O								8.2			8.4			8.4		8.4			

Chiseled Nos. 10-9 hearths.

Remarks: Cleaned flue to the hot fan.

in a deficiency of heat following any interruption and necessitated the intermittent use of gas on the bottom hearth at the approximate rate of 300 cu. ft. per hour.

In this connection it is pertinent to observe that roasters are capable of operation at tonnages roughly 50 per cent greater when connected to a stack, as compared with the same roaster connected rigidly to a chamber-acid plant, or any similar after process.

Operating labor for one unit of two roasters per 8-hr. shift consisted of one operator, one helper and one man to handle roasted ore. Additional day labor amounted to one chiseler per roaster, and one oiler-mechanic who also operated the green-ore conveying system. There was also available from the sintering plant one oiler-mechanic in the daytime, and one helper in the second shift. A shift foreman was in charge of both the roasting and sintering operations.

The day schedule, aside from repairs and changes in equipment such as feeders, consisted of chiseling two hearths per roaster, cleaning the hot fan, cleaning dust collectors and flues from the roaster to the fan on alternate days per roaster, stocking green ore in the roaster feed bins, and cleaning up. As necessary the flues from the hot fans to the Glover towers were cleaned.

Flue cleanings, which originally were returned to the roaster, were accumulated, and, by regulated feeder, fed into the ore cooler with the roasted ore, the sulphated flue dust being of more value in the sintering operation.

A log sheet for each roaster was kept, a typical log being reproduced in Table 3. This shows operation with four feeders, two on No. 1 hearth, and one each on Nos. 3 and 5 hearths, the ore being divided normally 50 per cent to No. 1 hearth and 25 per cent to each of the other two, tonnage for 24 hr. being 51.5 green ore, dry basis. The butterfly valves in the drier-hearth arms were open four points, and the bleeder valves at the top of the air-distributing headers were closed, all the cooling air being utilized. The air valves on the several hearths were open as shown, 14 turns being wide open, and on the bottom hearth the regulating sheaver is 4 in. open, 8 in. being wide open. Pressures are for the cooling-air supply duct, the top hearth and the hot fan, the latter being negative.

Regulation was based upon flue-gas analysis, made with an ordinary Orsat using caustic potash and pyrogallic acid. Emphasis was placed upon the oxygen content as a requirement of the acid plant, control being otherwise uncertain because of the high content of SO_3, as evidenced by opaqueness of the gas as drawn into the Orsat.

Sulphurs given are total, sulphate and sulphide, and represent the minus 10-mesh product. This ore contains a small amount of pellets from drying, which persist through the roaster, being only partly roasted. The sample does not include the morning product represented by lumps from the chiseling operation. Operation control by this analysis was found to be much more dependable than sulphurs of the total product.

TABLE 4.—*Characteristic Operating Results on Pecos Ore*
AUTOGENOUS ROAST ON GREEN ORE, DRY BASIS

Year of 1933	January		August		September	
Hearth	No. 3	No. 4	No. 3	No. 4	No. 3	No. 4
Rate, tons per day	59.3	59.3	48.85	48.85	57.7	57.7
Plus 10-mesh, per cent	10.5	13.58	3.93	5.28	4.86	6.27
Total sulphur	10.93	13.65	16.70	15.22	15.77	11.88
Sulphate sulphur	1.22	0.75	0.40	0.58	0.66	1.01
Minus 10-mesh, per cent	89.5	86.42	96.07	94.72	95.16	93.73
Total sulphur	2.44	2.88	2.80	2.48	2.74	2.64
Sulphate sulphur	1.92	1.81	0.76	1.47	1.32	2.12
Combined:						
Total sulphur	3.33	3.77	3.35	3.15	3.37	3.22
Sulphate sulphur	1.84	1.66	0.75	1.42	1.29	2.05
Product sinter feed:						
Total sulphur	3.35		3.18		3.10	
Sulphate sulphur	2.05		1.34		1.90	
Shrinkage, per cent	10.4		11.5		10.8	
Sulphur recovery, per cent	90.0		90.6		90.8	

January 1933:
- Ore distribution, 52 per cent No. 1 hearth, 26 per cent No. 3 hearth, 22 per cent No. 5 hearth.
- Air distribution, Nos. 4, 6, 8, 10 and 12 hearths.
- Average gas, 6.2 per cent SO_2 and 8 per cent O_2.
- Average hearth temperature, 1390° F.
- Rabbles: all large except hearths 6, 8, 10 of No. 4.

August 1933:
- Ore distribution, 59 per cent No. 1 hearth, 20.5 per cent No. 3 hearth, 20.5 per cent No. 5 hearth.
- Air distribution, Nos. 6, 8, 10 and 12 hearths.
- Rabbles: all large in No. 3, all small in No. 4.

September 1933:
- Ore distribution, 50 per cent No. 1 hearth, 25 per cent No. 3 hearth, 25 per cent No. 5 hearth.
- Air distribution, hearths 4, 6, 8, 10 and 12.
- Average gas, 6.2 to 6.4 per cent SO_2 and 8.2 to 8.4 per cent O_2.
- Hearth temperatures, 1350° to 1550° F. except No. 12.
- Rabbles: all large in No. 3, all small in No. 4.

The sulphur analysis of the feed to the sintering plant, designated as S-on, represents the sulphur of the production of both roasters of a unit, which also contains hearth accretions resulting from chiseling and cleanings from the roaster flues, the chiselings averaging 15.76 total sulphur and 15.60 sulphate sulphur. The ore was judged in practice by its appearance and development of heat when wetted. A dull brown color without sensible heat meant high sulphur without sulphate, while a bright brown to red, with development of so much heat when wetted that the ore could not be held in the hand, meant high sulphate and possibly high total sulphur; i.e., 4 or 5 per cent. Intermediate conditions meant less sulphate and less total sulphur. The operators became quite adept in forecasting sulphurs from this simple test.

Demand for both acid and ore varied between wide limits during the period under review, and entailed frequent drastic adjustments. In general, however, the operation proved flexible enough to meet these varying conditions, provided the equipment was maintained in a good state of repair. This applies particularly to the flue system, dust collector and hot fan, any openings in the flue system under high suction having an adverse effect on the operation, making control of air for roasting difficult, lowering the SO_2 tenor of the gas and overloading the acid head fan. Close cooperation is essential between the operators of the roaster and the acid plant, the two units being rigidly interconnected with but a minimum of gas leakage being tolerable, and that for short periods only.

Characteristic operating results under stated conditions are given in Table 4.

The effect of feeding ore at the end of a roast is indicated by a quotation from the operating report for the month of March, 1932, the February data being included for comparison of bottom feed (Table 5).

> "No. 4 roaster was operated throughout the month at the rate of 43 tons green ore daily. Normal feed was used with 50 per cent of the ore on No. 1 hearth, 25 per cent on No. 3 and 25 per cent on No. 5. On the first of the month a feeder was added on No. 9 hearth, feeding at the rate of 1.7 per cent of the ore feed in the upper part of the roaster. On the third this feed was increased to 2.1 per cent, on the fourth to 4.6 per cent and on the twenty-sixth to 6.3 per cent, the average being 4.66 per cent. The purpose of this feed on No. 9 hearth was to improve temperatures in the bottom of the roaster to effect better desulphurization."

Some of the conclusions that may be drawn from these data are obvious. In the first place, the operation is sensitive at low tonnages, though not difficult to control provided the flue system is tight and the hot fan in good operating condition, and something equivalent to this pertains to all operations. There are indications that autogenous operations can be maintained at inputs as low as 40 tons, that there is no question about operating in this manner at inputs of 45 tons and that the operation improves in stability at inputs up to 60 tons.

Optimum speeds for desired results are from 0.75 to 0.90 r.p.m., and this is limited by the depth of rabble load, in turn a function of the temperature with respect to the softening point at which the ore becomes sticky. Operating data presented are for speeds of 0.79, 0.87 and 1 r.p.m.

TABLE 5.—*Effect of Feeding Ore at End of Roast-Pecos Ore*
March, 1932

	No. 3	No. 4	No. 4 Feb.
Rate, tons per day	49.5	42.7	41.0
Plus 10-mesh, per cent	9.63	10.53	10.17
Total sulphur	9.21	11.89	9.08
Sulphate sulphur	1.33	1.36	2.09
Minus 10-mesh, per cent	90.37	89.47	89.83
Total sulphur	2.68	3.68	4.08
Sulphate sulphur	2.05	2.59	3.50
Combined:			
Total sulphur	3.31	4.54	4.59
Sulphate sulphur	1.98	2.46	3.36
Product sinter feed:			
Total sulphur		3.92	
Sulphate sulphur		2.94	
Shrinkage, per cent		8.15	
Sulphur recovery, per cent		88	

Distribution of the ore effects favorable modification of the temperature gradient, which conforms closer to the average value than when the ore is fed entirely into the top hearth. Because of production requirements, the possibilities here were not fully explored, but it is not at all impossible that more extensive distribution of ore with a smaller proportion on No. 1 hearth might be advantageous, resulting in a more even heat gradient. Pecos ore will "snowball" at 900° C. pyrometer reading and stall a roaster.

Distribution of air is very flexible. It was found that the bulk of the air could be moved from the bottom up to and including Nos. 4 and 6 hearths without affecting SO_2 content, but it is preferable to admit most of the air into Nos. 10, 8 and 6 hearths in that order, with sufficient air admitted into No. 12 hearth to satisfy the draft there. Where sulphur is high the admission of air increases temperature, thus admission of air into No. 4 hearth raises temperatures in that zone. Distribution of air also increases formation of sulphates and promotes the sulphate-sulphide reaction within the ore bed on the hearth.

The smaller rabbles have the effect of increasing the formation of sulphates, and, other conditions being equal, reducing the percentage of plus 10-mesh oversize and the sulphur content of roasted ore. This result is very much to be desired, it having been amply demonstrated that a roast of the type produced—i.e., a high percentage of the total sulphur as sulphate—must be of this character for satisfactory sintering, and if not of this character may be but partially sinterable, or must be sintered twice for producing an acceptable sinter. Sintering is not, however, the subject of this paper and will not be discussed further here, though it may be observed that an appreciable flavoring of the requirements of Rigg's process is necessary in sintering after that of Baelen.

The book record for the year 1931 shows clearly over-all results in treating several different ores and mixtures at widely varying rates, governed by acid demand:

	Weight	Zinc	Sulphur
Green ore, lb	79,876,277	43,412,895	24,399,908
Roasted ore, lb	70,026,444	42,828,947	2,592,806
Loss (shrinkage and dust), lb	9,849,833	583,948	21,807,102
Loss, per cent	12.33	1.34	89.37

While Pecos was the basis of operations and accounted for the bulk of production, other ores were treated alone and later certain of them mixed with Pecos. Analyses of several are given in Table 6. Of these, ore B, which is a complex zinc-iron sulphide, largely marmatite, did not roast to the required sulphur without extraneous fuel, though the use of natural gas at the rate of 300 cu. ft. per hour with a 45 to 50-ton feed resulted in a dead roast. This ore was roasted successfully mixed with Pecos, though with more difficulty than Pecos alone. The other ores were all successfully roasted alone, but because of the difficulties attendant on the heavy fuming characteristics of the high-lead ores it became the practice to mix them with Pecos unless cadmium values necessitated segregation and saving of the fume.

TABLE 6.—*Analyses of Various Ores*

Ore	Percentages							
	Zn	S	Fe	Pb	CaO	MgO	Cd	Ag
Pecos	54.2	30.4	6.5	1.37	0.55	0.69	0.10	3.34
A	57.6	30.7	1.3	2.15	1.40	1.05	1.08	20.90
B	57.5	30.3	5.8	0.52	0.66	0.50		
C	57.3	31.6	4.1	1.54	0.43	0.36	0.83	13.57
D	56.1	29.9	2.45	2.00	0.79	0.58		17.25
E	55.4	31.2	4.9	2.30	0.20	0.14		3.30

How Joplin and Tennessee flotation concentrates would roast in these roasters is not known. Laboratory tests showed that they roast somewhat more easily than Pecos, therefore it is possible that they would roast satisfactorily without extraneous fuel.

Flotation concentrates, or concentrates ground to 100 per cent minus 20-mesh and containing a large amount of fines, are the only zinc ores that can be expected to roast in a comparable manner.

Pecos ore contains approximately 1.5 per cent copper and this copper as oxide is sufficient in its catalytic function to produce sulphate sulphur in the roast, partly, if not wholly, at the expense of sulphide sulphur.

The book record for the year 1931, above, indicates a low dust loss. To some extent this is an arbitrary figure and is based upon scale weights, dry basis, of green ore entering the plant, and of sinter produced, and includes losses in drying and handling. The total unaccounted zinc amounted to 1.77 per cent, of which 1.34 per cent was allocated to roasting. This is equivalent to slightly less than 2.50 per cent ore basis, and is a net figure reflecting salvage of flue dust. Dust carried out of the roaster amounted to approximately 3 per cent compared with an originally assumed 5 per cent and a usual 7 to 9 per cent, the anticipated decrease having been based upon the method of feeding the ore. In the first place the feed is continuous, not a batch periodically dropped on a thick ore bed close to the gas offtake, and in the second place the feed is at the level of the ore bed without drop, so that little dusting results. The ore also is dry and hot, so that there are no moisture explosions.

In selection of dust collectors, laboratory tests were made by the manufacturer, using samples from the Hegeler kilns, and this was followed by service tests made by the author with a field outfit. These tests indicated recoveries of 87 to 90 per cent at optimum inlet velocities running hot, compared with the manufacturer's results of 97 to 99 per cent cold.

After installation, weighed products of the dust collector amounted to 2380 lb. in 23½ hr., that being the continuous operating period.

TABLE 7.—*Analyses of Flue Dust*

Assays	Dust Collector, Per Cent	Flue to Fan, Per Cent	Flue to Acid, Per Cent
Zn	49.1	25.2	31.8
Cd	0.205	0.63	0.62
Pb	2.16	18.41	13.40
Cu		0.66	0.73
Fe		3.95	4.85
Ag, oz		3.76	3.68
S	22.00	15.92	15.42
Zn (soluble)		21.6	21.4

This is equivalent to return of 110.7 lb. per hour, or 2.2 per cent of the ore rate.

In a more complete test made by Cottrell representatives, sampling was done in the flue between the collector and the fan, no determinations being made of the dust carried out of the roaster. Concurrently the collector dust was weighed and amounted to 42 lb. per hour. Dust actually fume, collected in the sampling apparatus indicated a loss of 31.7 lb. per hour. Respective values were 49.1 Zn, 2.16 Pb and 19.8 Zn, 29.35 Pb. However, the dust recovered represented 1.096 per cent of the roaster feed and the fume loss 0.828 per cent. If any great dust loss had been present the latter figure would have been much higher. Actual flue-dust analyses are given in Table 7.

Assuming sulphur combined with zinc to be soluble sulphate, and distributing the sulphur as sulphate, it is found that sulphate formation follows the formation temperatures rather closely, the order being lead, cadmium, zinc, copper and iron. The early deposition of lead supports this and explains the characteristic flue deposits from high-lead ores. The orange color of Pecos fume indicated the presence of iron oxide and lends further support. Samples taken at the dust chamber of the Glover tower would probably have shown further progress of this action. An analysis of acid when treating ore showed: Zn, 0.0515 per cent; Cd, 0.0513; Pb, 0.0372.

It can be safely stated that the dust losses are low and well within the 5 per cent design figure; in fact, under 3 per cent ore basis.

A survey of No. 4 roaster, which operated at an average input of 24 tons of ore daily with brimstone burned on No. 11 hearth at the rate of 8 tons daily, is given to indicate the effect of such practice, Dewey having done somewhat the same thing some 25 years ago. (Table 8.)

The ore tonnage was very low, the roaster being operated in this manner temporarily in preference to shutting it down. What the results would have been with normal tonnage is not known.

In this operation no difficulty was experienced in feeding and burning the brimstone. Observation indicated that the brimstone, while it melted and formed a pool, was completely volatilized and burned in one-fourth of the hearth area. Conclusions can be only indicative, the ore tonnage being too low for any normal operation. It is apparent that brimstone burned in this manner increases sulphate formation, which is desirable in promoting the hearth reaction, but that it should not be burned at any one point to raise temperatures much above the lower limit of sulphate dissociation, 755° C., in a preroasting operation followed by sintering. This effect is observable in the sampling of No. 11 hearth, though the high total sulphur shown is undoubtedly due to contamination by unconsumed brimstone, and the true composition of the ore on this hearth is quite different from that given, as is evidenced by the analysis of the sample from No. 12 hearth.

It appears reasonable to conclude that the use of brimstone will promote the desired results, and that the character of the roaster product can be controlled by varying the amount of brimstone burned and by introducing it at more than one hearth to control temperatures; in this instance on No. 9 hearth or both 9 and 11.

TABLE 8.—*Survey of No. 4 Roaster*

ORE AND BRIMSTONE

Hearth No.	Temperature, Deg. F.	Mesh	Screen, Per Cent	Sulphur, Per Cent		Combined, Per Cent		Loss, Total S
				Total	Sulphate	Total S	Sulphate S	
1	1270	+10	20.2	28.70	0.16	28.85	0.21	1.15
		−10 + 20	5.6	28.74	0.18			
		−20	74.2	28.93	0.22			
2	1420	+10	12.1	25.20	0.19	27.10	0.28	1.75
		−10 + 20	6.0	25.98	0.20			
		−20	81.9	25.75	0.30			
3	1340	+10	11.0	21.92	0.32	17.93	0.38	9.17
		−10 + 20	6.7	22.71	0.17			
		−20	82.3	17.13	0.40			
4	1380	+10	12.5	25.04	0.06	19.19	0.34	+1.26
		−10 + 20	6.3	24.26	0.14			
		−20	81.2	19.29	0.40			
5	1310	+10	13.0	22.08	0.36	12.75	0.59	6.44
		−10 + 20	6.7	19.13	0.35			
		−20	80.3	11.04	0.65			
6	1350	+10	15.5	21.12	0.57	11.68	0.66	1.07
		−10 + 20	6.7	18.72	0.27			
		−20	77.8	9.20	0.71			
7	1320	+10	13.0	17.68	1.47	6.91	1.40	4.77
		−10 + 20	7.0	12.72	1.08			
		−20	80.0	4.56	1.42			
8	1310	+10	14.2	14.64	1.80	5.53	2.19	1.38
		−10 + 20	6.5	8.16	1.52			
		−20	79.3	3.68	2.29			
9	1300	+10	14.5	11.52	4.17	6.27	4.67	+0.74
		−10 + 20	6.5	6.40	3.78			
		−20	79.0	5.32	4.83			
10	1460	+10	14.2	8.24	4.82	5.80	5.24	0.47
		−10 + 20	7.0	5.04	4.67			
		−20	78.8	5.56	5.37			
11	1470	+10	23.2	18.08	0.66	13.23	0.97	+7.43
		−10 + 20	7.2	10.52	1.20			
		−20	69.6	10.31	1.06			
12	1090	+10	14.3	7.40	2.32	3.88	1.99	9.35
		−10 + 20	7.3	4.52	2.57			
		−20	78.4	3.05	1.88			
Product		+10	14.7	9.18	2.78			
		−10	85.3	3.89	2.67			
Combined				4.65	2.69			
Average for month				4.45	2.57			

Such a process would be particularly applicable to the refractory class of ores as represented by ore B, and might prove advantageous in the roasting of Joplin and Tennessee ores, and any concentrates too coarse to be amenable to treatment in the process under discussion.

To explore the progress and characteristics of desulphurization, hearth samples were taken in January 1932, when a mixture of ⅔ Pecos ore and ⅓ ore E was in process, and when the other of the two roasters of the unit was operating partly on ore and partly on brimstone, a condition that made control difficult. The data, however, are illustrative of the process with these modifications. The samples were grab samples taken about 24 in. inside the side walls, so that, numbering from the top down, samples from the even hearths represented passage over two hearths and one drop, while samples from the odd hearths represented to some extent the effect of the ore falling through the drop hole. At the time, 55 tons of ore was in treatment, 27.5 tons into No. 1 hearth and 13.75 tons each into Nos. 3 and 5 hearths, with collector dust into No. 7. Air distribution, based upon valve opening without regard for internal negative roaster pressures, was 16.9 per cent into No. 4 hearth, 25.31 per cent each into Nos. 6, 8 and 10 hearths, and 7.16 per cent into No. 12 hearth.

Samples were screened and sulphurs determined for plus 10-mesh, minus 10 plus 20, and minus 20-mesh. Screen test variations were unquestionably due to "snowballing" of the fines on agglomerated pellets, the green ore screening 8.3 per cent minus 10-mesh, 6.7 per cent minus 10 plus 20-mesh and 85 per cent minus 20-mesh, and the roasted ore 7.2 per cent minus 10-mesh, 6.7 per cent minus 10 plus 20-mesh and 86.1 per cent minus 20-mesh.

The sulphurs show clearly that roasting is effective, below rather high sulphur limits, in the fines through 20 mesh, and that the formation of sulphates, desired in the following sintering operation, is confined almost entirely to the fines. This is strikingly noticeable on hearth No. 10, through a combination of air with a temperature of 1390° F., which coincides with Hofman's temperature of dissociation of sulphate, 755° C. The loss of this sulphate with accompanying decrease in sulphur suggests the sulphate-sulphide hearth reaction. Table 9 presents this survey.

Through the courtesy of B. N. Zimmer, of The American Metal Co. Ltd., a survey of No. 3 roaster operating on Pecos ore was made in August 1936. The data obtained are shown in Table 10 and illustrated by the graphs in Figs. 4 and 5.

While sampling is necessarily faulty, there being some danger of catching lumps or scale, and, having to be done quickly through an open door normally closed, fines in the ore may be lost because of air currents set up, more so in sampling the outer drop holes immediately in front of the doors, still the data bring out interesting information. These data may be more readily followed by means of a table showing the magnitude

TABLE 9.—*Survey of No. 3 Roaster*
TWO-THIRDS PECOS ORE, ONE-THIRD ORE E

Hearth No.	Temperature, Deg. F.	Mesh	Screen, Per Cent	Sulphur, Per Cent		Combined, Per Cent		Loss, Total S
				Total	Sulphate	Total S	Sulphate S	
1	1190	+10	17.9	26.56	0.03	26.05	0.11	3.95
		−10 + 20	6.1	27.20	0.05			
		−20	76.0	26.96	0.13			
2	1440	+10	19.0	19.84	0.19	21.95	0.23	4.97
		−10 + 20	4.9	23.28	0.14			
		−20	76.1	22.40	0.25			
3	1250	+10	9.6	25.04	0.21	23.25	0.40	+1.30
		−10 + 20	6.0	24.25	0.29			
		−20	84.4	23.12	0.42			
4	1460	+10	7.9	24.25	0.26	21.57	0.46	1.68
		−10 + 20	6.2	24.49	0.27			
		−20	85.9	21.12	0.49			
5	1230	+10	10.0	19.76	0.43	18.28	0.45	3.29
		−10 + 20	6.4	23.44	0.25			
		−20	83.6	17.70	0.47			
6	1390	+10	8.4	22.96	0.23	18.14	0.46	0.14
		−10 + 20	6.2	23.84	0.24			
		−20	85.4	17.36	0.50			
7	1420	+10	10.2	22.56	0.50	12.04	0.66	6.10
		−10 + 20	7.0	17.60	0.47			
		−20	82.8	11.28	0.69			
8	1390	+10	9.0	18.92	0.44	13.87	0.56	+1.83
		−10 + 20	6.2	19.36	0.40			
		−20	84.8	12.92	0.59			
9	1360	+10	9.7	21.88	0.16	12.34	0.50	1.53
		−10 + 20	7.0	20.52	0.17			
		−20	83.3	10.64	0.52			
10	1390	+10	7.2	17.28	1.35	9.91	1.69	2.43
		−10 + 20	17.0	13.89	4.48			
		−20	75.8	8.32	1.10			
11	1360	+10	8.2	18.80	0.10	7.02	0.43	2.89
		−10 + 20	7.0	15.88	0.19			
		−20	84.8	5.16	0.48			
12	1080	+10	7.2	19.51	0.28	6.35	0.68	0.67
		−10 + 20	6.7	15.32	0.31			
		−20	86.1	4.54	0.73			
Product.		+10	9.2	15.44	0.76			
		−10	90.8	3.02	0.87			
Combined.				4.16	0.85			
Average for month.				3.88	1.47			

of changes taking place, consolidating the data to stress the progress of the process (Table 11).

Recalling that the odd-numbered hearths are "in" hearths, the center drop holes are 1-2, 3-4, etc., and the outer drop holes 2-3, 4-5, etc. The increases shown in total and sulphide sulphurs of the outer drop holes probably do not occur, for reasons given above, and may be disregarded.

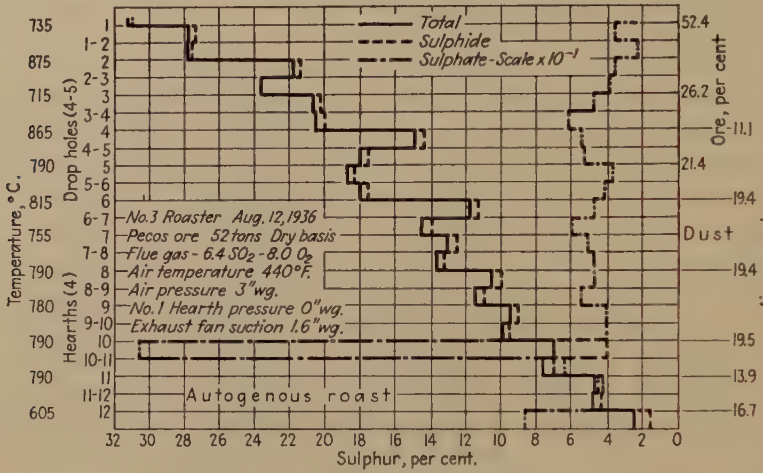


FIG. 4.—SURVEY OF NO. 3 ROASTER OPERATING ON PECOS ORE.

It appears from Table 11, and also from the graphs, that drop-hole effect is practically negligible within the time interval existing, until No. 10 hearth is reached, unless sulphates are formed in suspension and immediately lost in the sample by reaction with sulphides. It seems reasonable to conclude that the desulphurization is almost exclusively

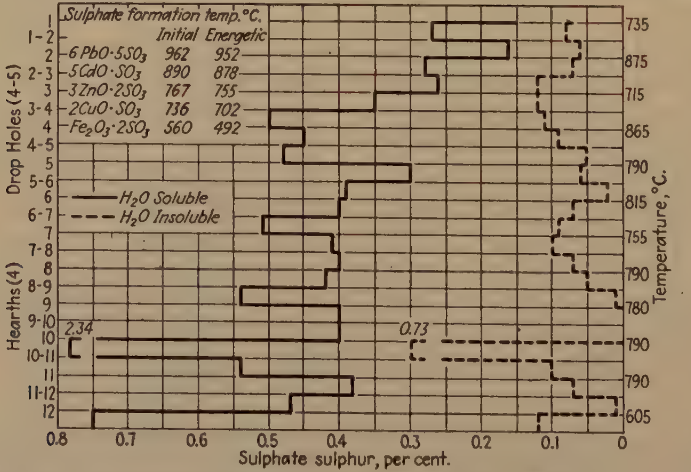


FIG. 5.—OCCURRENCE OF SULPHATE SULPHURS IN ROASTING PECOS ORE.

a hearth reaction at temperatures above the formation temperature of zinc sulphate.

TABLE 10.—*Survey of No. 3 Roaster, Aug. 12, 1936*

PECOS ORE

Hearth No.		Sulphur, Per Cent			H_2O Solubility	
		Total	Sulphate	Sulphide	Soluble S	Insoluble S
1	On[a]	31.20	0.22	30.98	0.15	0.07
1	Off	27.70	0.35	27.35	0.27	0.08
2	On	27.80	0.22	27.58	0.16	0.06
2	Off	21.70	0.35	21.35	0.28	0.07
3	On	23.60	0.38	23.22	0.26	0.12
3	Off	20.60	0.47	20.13	0.35	0.12
4	On	20.50	0.61	19.89	0.50	0.11
4	Off	14.80	0.54	14.26	0.45	0.09
5	On	17.92	0.53	17.39	0.48	0.05
5	Off	18.64	0.36	18.28	0.30	0.06
6	On	17.92	0.41	17.51	0.39	0.02
6	Off	11.68	0.47	11.21	0.40	0.07
7	On	14.52	0.60	13.92	0.51	0.09
7	Off	12.92	0.51	12.41	0.41	0.10
8	On	13.68	0.47	13.21	0.40	0.07
8	Off	10.44	0.47	9.97	0.42	0.05
9	On	11.50	0.55	10.95	0.54	0.01
9	Off	9.40	0.40	9.00	0.40	0.00
10	On	10.00	0.40	9.60	0.40	0.00
10	Off	7.06	3.07	3.99	2.34	0.73
11	On	7.70	0.64	7.06	0.54	0.10
11	Off	4.70	0.45	4.25	0.38	0.07
12	On	4.81	0.48	4.33	0.47	0.01
12	Off	2.43	0.87	1.56	0.75	0.12

[a] Samples noted "off" were taken on the hearth at the edge of the respective drop holes, and samples noted "on" were taken at the end of the drop from hearth to hearth and just before reaching the succeeding hearth. The on-off difference then represents the hearth effect, while the off-on difference represents the drop-hole effect.

Fig. 4 indicates that hearth roasting proceeds rapidly down to hearth 6, except as it is apparently retarded on hearth 5 by ore fed there, and that the air-admission hearths show an increased rate of desulphurization. From hearth 7 down, roasting proceeds at a retarded but uniform rate.

Fig. 5 shows the occurrence of sulphate sulphurs. The amounts are so small as to cast suspicion on their being present, and they do disappear on hearth 9 where sulphur content is lower. It is possible that sulphate sulphur formed in the cooling of the sample.

TABLE 11.—*Sampling*

Hearth No.	Ore, Per Cent	Air, Per Cent	Sulphur, Per Cent			
			Soluble Sulphate	Insoluble Sulphate	Sulphide	Total Sulphur
1	52.4		+0.12	+0.01	−3.63	−3.50
1-2			−0.11	−0.02	+0.23	+0.10
2			+0.12	+0.01	−6.23	−6.10
2-3			−0.02	+0.05	+1.87	+1.90
3	26.2		+0.09	0.00	−3.09	−3.00
3-4			+0.15	−0.01	−0.24	−0.10
4		11.1	−0.05	−0.02	−5.63	−5.70
4-5			+0.03	−0.04	+3.13	+3.12
5	21.4		−0.18	+0.01	+0.89	+0.72
5-6			+0.09	−0.04	−0.77	−0.72
6		19.4	+0.01	+0.05	−6.30	−6.24
6-7			+0.11	+0.02	+2.71	+2.84
7	Dust		−0.10	+0.01	−1.51	−1.60
7-8			−0.01	−0.03	+0.80	+0.76
8		19.4	+0.02	−0.02	−3.24	−3.24
8-9			+0.12	−0.04	+0.98	+1.06
9			−0.14	−0.01	−1.95	−2.10
9-10			0.00	0.00	+0.60	+0.60
10		19.5	+1.94	+0.73	−5.61	−2.94
10-11			−1.80	−0.63	+3.07	+0.64
11		13.9	−0.16	−0.03	−2.81	−3.00
11-12			+0.09	−0.06	+0.08	+0.11
12		16.7	+0.28	+0.11	−2.77	−2.38

The phenomenon occurring on No. 10 hearth is characteristic. A large volume of air is admitted here, the sulphur content is comparatively low and the temperature is above the dissociation temperature of zinc sulphate. Both water-soluble and insoluble sulphurs increase greatly, the former from 0.4 to 2.34 per cent and the latter from 0 to 0.73 per cent. This is accompanied by a drop in total sulphur of 3 per cent, and is followed by notable drops in sulphur on hearths 11 and 12, these being of the order of ⅓ to ½ the remaining sulphur.

The action on No. 12 hearth is readily explainable in the sulphide-sulphate reaction, the temperature being such as to promote sulphate formation. That on No. 10 hearth is undoubtedly due to the large amount of air admitted, which, at 450° F., follows hydraulic principles and blankets the ore bed, thus reducing the surface temperature sufficiently to promote active sulphate formation. The temperature of the ore was not taken, and may well be 20° to 40° C. below that of the hearth atmosphere, which was measured. The sulphate thus formed, and not consumed in the hearth reaction, is dissociated in the 10-11 drop-hole effect, yielding SO_3, which returns and sustains sulphate formation on that hearth. Water, of which a total of some 4 lb. a minute accompanies the air, may enter the reaction also.

The hydraulic principle with respect to air as utilized applies where air is admitted, but the sulphate thus formed is immediately used in the hearth reaction where sulphurs are higher and is consequently absent in samples.

What reactions definitely occur in roasting is debatable. The author has believed the roasting process to be two-stage and double, and this seems to be borne out in this operation where the issue is not clouded by extraneous fuel. The reaction is probably a stage of sulphate formation represented by the two reactions $ZnS + 2O_2$ and $3ZnO{\cdot}2SO_3$, followed by the hearth reaction $3ZnSO_4 + ZnS = 4ZnO + 4SO_2$. This may be partly drop-hole effect, but is certainly principally hearth reaction.

Examinations of roasted ore representing the whole product as sintering-plant feed disclosed the presence of both basic and water-soluble zinc sulphate, the normal ratio being about 1:1 and varying directly as a function of the total sulphur; the proportion, but not the quantity, of basic sulphur increasing with total sulphur.

Analyses of flue dust, taken where temperatures are below that of dissociation of zinc sulphate, show contents of 21.6 per cent soluble out of 25.2 per cent total zinc, and 21.4 per cent out of 31.8 per cent total. Sulphide sulphurs were 1.51 and 1.82 per cent respectively, which leaves 0.31 and 6.44 per cent zinc as basic sulphate. Something of this nature may take place where the air admitted blankets the hearth.

Thorpe gives a number of basic sulphates, 2, 3 and 5 $ZnO{\cdot}SO_3$, while Mellor affirms the reaction $ZnO{\cdot}SO_3$. Maier gives the complete reaction as $2ZnS + 2O_2 = 2ZnO + SO_2$, and concludes this to probably result from consecutive reactions $ZnS + 2O_2 = ZnSO_4$, $ZnSO_4 = ZnO + SO_3$ and $SO_3 = SO_2 + \frac{1}{2}O_2$.

The developments of Fulton in suspension roasting some years ago, wherein the product was largely sulphate, and the down-draft roasting of Coolbaugh are instructive in an analysis of this question.

In Pecos ore the copper content as oxide definitely does promote sulphate formation, either directly as a catalyst or indirectly in converting SO_2 to SO_3. Iron also has this effect when oxidized to Fe_2O_3. Judging by the color of roasted Pecos ore, however, and based on experience, the roast must approach a sulphur content under 3 per cent before ferric oxide forms, and under such conditions the remaining sulphur may be nearly all sulphate.

Operating costs are interesting, though the lowest possible costs were never realized, the production schedule never having demanded operation of all four roasters, either in number or tonnage (Table 12).

The installation of these roasters effected several economies and avoided expected additional investment. Recoveries of sulphur returned to a level somewhat higher than had obtained in roasting normal concentrates in the Hegeler kilns, the gases were stronger, being higher in SO_2 content and carrying an appreciable amount of SO_3, thus reducing niter consumption. Reduction of dust losses was considerable and operating difficulties were much relieved. Decrease in the volume of gas from that of the Hegelers, and also a smaller volume than would have been, and is necessary when using extraneous fuel, released tower and chamber space and increased the capacity of the acid plant to make it unnecessary to further consider an expenditure for that purpose.

TABLE 12.—*Operating Costs of Roasting Pecos Ore*, 1933

Month	Roasters Operating	Green Ore, Tons	Cost per Ton
January	2	3,416	$0.729
February	2	2,768	0.756
March	2	3,493	0.774
April	2	3,407	0.678
May	2	3,492	0.71
June	2	3,118	0.83
July	2	3,275	1.175
August	2	3,472	0.853
September	2	3,581	0.776
October	2	2,977	1.017
November	2	3,048	1.114
December, 5 days	2	464	1.565
Adjusted cost for year	2	36,744	0.856

The type of roast produced, containing sulphate found necessary for satisfactory sintering, could not have been produced as desired by any roaster then known, with the possible exception of the O.R.D. roaster, though not well suited to ore of the character to be treated, and perhaps the Coolbaugh roaster as well, since all required extraneous fuel for reduction of sulphurs to the required content, and consequently operated at temperatures above the dissociation temperatures of such sulphates, and this situation is unchanged today, so far as the author knows.

In 1927–1928, others were developing plans along parallel lines to solve similar problems as modified by local requirements, principally with respect to ores to be treated. All of these roasters were departures from customary practice in point of size, being of 12 to 16 hearths, the roasters of Queneau at Donora being distinguished by the number of hearths, 16, and the adoption of brimstone as extraneous fuel, the brimstone being fed to burners as liquid and admitted into the roaster as vapor. Of this group the roasters at Langeloth went into production first, closely followed by East St. Louis, Donora and Rosita, possibly not in that order, and somewhat later by Moundsville.

The subject is still very much alive, and it is hoped that this paper may contribute something of value, particularly to the question of hearth roasting versus flash roasting, or suspension roasting, of zinc ores.

Horizontal Retort Practice of the National Smelting Company, Limited, Avonmouth, England

By T. B. Gyles*

Zinc is made by the National Smelting Co. and its associates by both the horizontal retort process and the vertical retort process developed by the New Jersey Zinc Co. This paper deals only with the horizontal retort practice at Avonmouth.

That the horizontal retort process does survive in all countries in some form or other is due to at least partial success in overcoming some of the inherent difficulties of the process. The horizontal retort furnaces ran into considerable difficulties when the product of the selective flotation of mixed lead and zinc ores became the normal material for treatment. It is necessary, therefore, to make some reference in connection with the process to the preliminary treatment of the ore prior to distillation. Therefore we include some small reference to this aspect in our description.

Fig. 1.—General view of Avonmouth Works.

Furnace Design and Structure

Of the types of furnaces in operation at the company's various works, those at Avonmouth are perhaps more typical of the trend to utilize large units, with a subsequent saving in costs, such as heating and supervision.

Manuscript received at the office of the Institute Aug. 6, 1936.

* Manager, Technical Department, The National Smelting Company, Limited, England.

Such advantages, of course, are offset by less detailed control in a process where every retort is, in fact, a small separate unit.

There are four Avonmouth furnaces, each of which produces approximately 12.25 tons of metal per day. There are 384 retorts per furnace; each side having four rows of 48 retorts each. The furnace is divided into four main sections, each of which has its own separately controlled gas and air systems, but all connected to the common live gas main and common waste-gas flue. The furnace is of the Rhenish type and the maximum temperature attained in the system is 1400° to 1430° C., which is lower than that used at one time but is sufficiently high for the use of regenerators and to permit the use of waste-heat boilers.

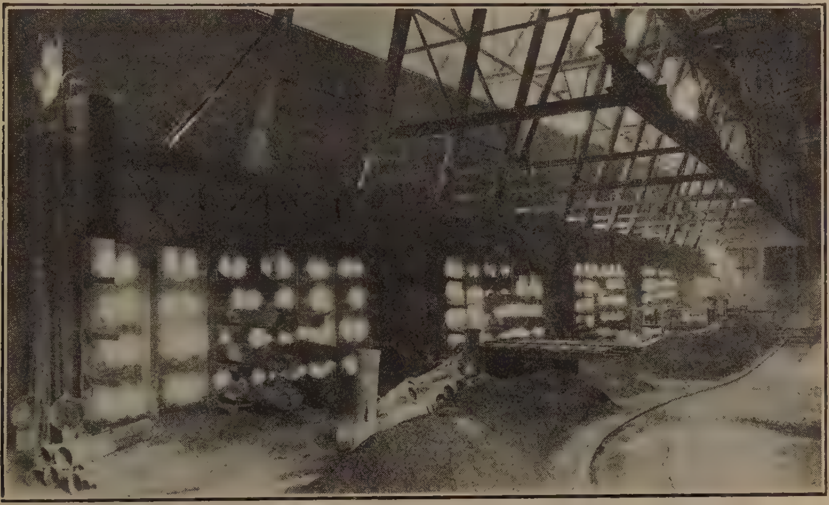


FIG. 2.—EXTERIOR VIEW OF FURNACE.

The furnace is "reversed" every 20 minutes and thus the waste gases pass alternately through the two regenerator settings. The air reaches the combustion chamber at about 1000° C. The waste gases leaving the regenerators have a temperature of about 600° C., and are then passed under specially designed boilers to provide steam for the producer-gas plant and elsewhere.

The furnaces are repaired one section at a time, and the average life of the furnace as a whole may be taken as 4 to 5 years. This is a considerable improvement on the 2½ years that was the usual life before the introduction of new roasting practice to be described later.

RETORT COMPOSITION AND MANUFACTURE

The size of the retorts has been considerably increased in recent years; at present, they have a capacity of the order of 2.86 cu. ft. The inside dimensions are approximately 8 by 11 by 5 ft. 5 in. long. There are very few larger retorts in operation elsewhere.

There is a limit to the dimensions to which a retort can be made: (1) because of the structure of the furnace itself; (2) the difficulty of driving heat through to the center of the charge increases as retort diameter is increased; (3) there is a limit to the length and capacity that workmen can cope with; and (4) when the distillation period is confined to, say, 20 hr. of the day, there are practical limits to the amount of metal that can be distilled over.

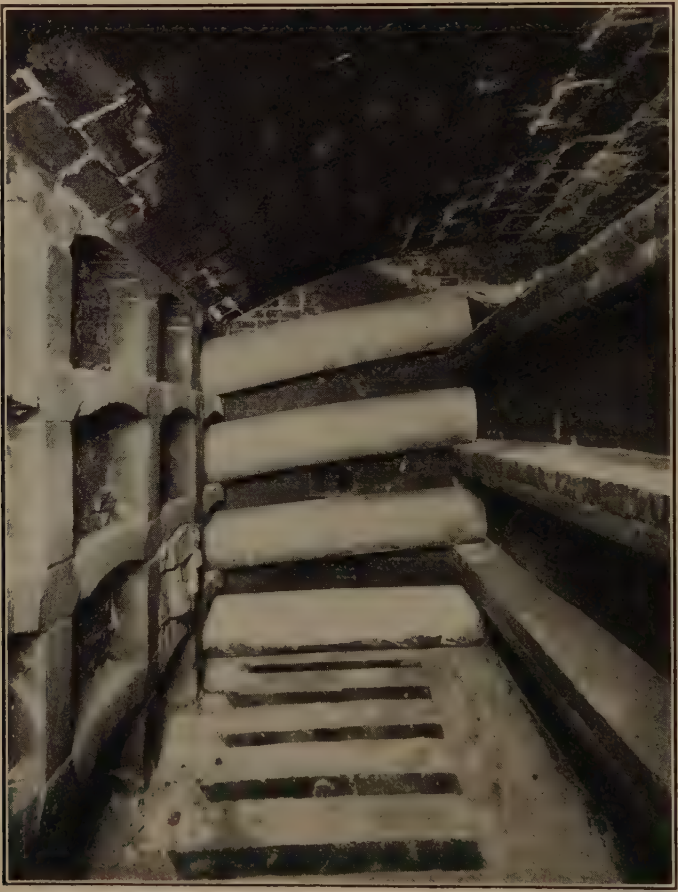


Fig. 3.—Interior of furnace, showing retorts in position.

Retorts should have flawless structure, low porosity and high refractoriness. There has been considerable research in the pottery section as to the type of clays to be used. Much depends on the type of ore to be treated, and as mentioned later, the sintering process developed by this company has materially assisted in raising the retort life to the order of 40 days. Nevertheless, careful retort manufacture is an important factor in this improved life.

The retort mixture consists of roughly equal proportions of plastic, semiplastic, and calcined clays, together with a small quantity of coke. Although it is unwise to base too much importance on the average chemical analysis of a refractory mixture, the composition is approximately: SiO_2, 62; Al_2O_3, 23.4; coke, 3.2 per cent.

The pottery practice involves the well-known procedure of mixing, rotting, pugging and extrusion. Research is continually taking place not only with a view to improvement in the retort itself, but also with a view to making the best use of clays available within the country. The condensers are also made in the pottery from a mixture made up of 50 per cent crushed retorts and 50 per cent plastic clay.

ORE PREPARATION

The ore treated at Avonmouth consists entirely of sulphide ores originating in Australia, Newfoundland and elsewhere. Originally these ores were roasted in hand-rabbled Delplace furnaces, and later in the Rigg two-stage process, whereby the material was partially roasted in mechanical hearth furnaces and finally desulphurized by sintering on a Dwight-Lloyd machine. The present process is one developed at Avonmouth, whereby the sulphide ore is directly sintered. In effect, the raw ore is diluted with approximately five times its weight of already sintered material, the optimum mixture conditions being about 5.5 per cent sulphur content with particle size of the order of ⅛ in. This process delivers sulphurous gases with a 6 per cent SO_2 tenor, and the sintered product averages 0.25 per cent S. Not infrequently routine assays record only a trace of residual sulphur. The zinc loss of the process is from 1 to 1.5 per cent.

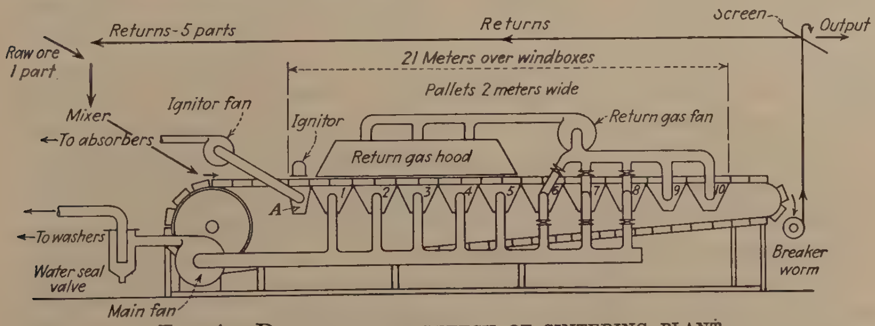


Fig. 4.—Diagrammatic sketch of sintering plant.

Many difficulties were encountered before this process was established, particularly as it was necessary to use all the sulphurous gases for acid manufacture. Sintering units producing over 200 tons of sintered ore per day now work efficiently in conjunction with contact acid plants developed by the company.

The effect of the improved physical condition of the roasted ore, i.e., the sintered ore, has been very influential in the distillation process. The furnaces now operate at a lower temperature than hitherto and yield greater amounts of metal, with higher efficiencies. It would be fair to say that the furnace temperature gradient has been lowered to an extent equivalent to at least 100° C. at the maximum. The cumulative effect of this and other improvements over the last two decades has increased the recovery by 10 per cent. The recovery ranges from 89 to 93 per cent, and the output per furnace has been more than doubled.

Charge and Maneuver Operation

The charge for the furnace is made up as follows. Anthracite duff to the extent of 36 to 37 per cent by weight of the sintered ore is added to the sintered ore, together with a regulated amount of crushed condensers corresponding to those withdrawn from service the previous day. The whole is well mixed and laid on the operating floor ready for the day's work. Blue powder collected in the prolongs from the distillation of the previous charge, together with "fronts," to be described later, is dumped on the charge and mixed during the charging operation. The maneuver period itself takes 2½ to 3 hr. The work commences each morning by the men cutting out, removing and replacing all defective retorts that were marked down for extraction on the previous day, or which have been found leaking badly during the night. The number of new retorts required were placed in an annealing stove the day before and brought to a temperature of 800° to 900° C. in readiness for the morning. The number changed varies widely according to conditions and with varying ores. As this is accomplished, the condensers are tapped finally for any remaining metal, preparatory to being cut down and removed from the mouth of the retort. About six inches of the old charge in the front of the retort, from which the zinc has been only partially eliminated, and known as "fronts," together with the clay adhering to the retort, are removed and placed back on the fresh charge.

The task of stirring out the old, worked-off charge is now commenced, the residue falling through holes in the floor into bins below, from which it is subsequently removed either for washery treatment or to the dump. Of recent years, improved flotation practice at the mines tends to render the treatment of residues unremunerative.

It is very necessary that the retorts shall be stirred out as completely as possible and all slag removed. The fresh charge is now thrown nearer the face of the furnace, preparatory to charging into the retorts. The furnace is then tested; i.e., the retorts are examined for leakages. This is done by lowering the main drafting damper and turning the producer gas full on, thus creating a pressure in the combustion chamber. Holes or cracks in the retorts are indicated by spurts of flame entering through them. Defective retorts are patched or removed next morning. The badly damaged ones are not charged.

Charging of the furnace then commences, by scoop and puncher. The charge is flung into the retorts by the maneuvermen, and compressed tightly by repeated blows with the iron rammer or puncher. When the furnace is completely charged, the condensers are placed at the mouth of the full retorts and the joints are sealed with wet clay firmly pressed in with a hot iron. To the ends of the condensers iron prolongs are attached, designed to trap any uncondensed zinc, in the form of blue powder. The furnace is then handed over to the control staff for the distillation period.

Distillation Period and Condensation

The furnace is brought rapidly up to the temperature at which distillation begins; say, 1000° C. During this period the elimination of volatiles from the reducing material proceeds. The furnace is then set back; i.e., the supply of gas and air is reduced to that sufficient to maintain a steady distillation rate. From this point onwards the temperature is gradually raised to maintain this steady distillation rate, which itself must be compatible with efficient condensation.

The control throughout the distillation period is a question that has occasioned much trial and thought. Much depends on the judgment of the foreman in charge of the furnace, and he takes into account the size, color and condition of the carbon monoxide flames, which burn at the mouth of the condensers. This is often deceptive. Originally at Avonmouth the condensers were tapped five times during the course of the distillation period and the amount of metal withdrawn was a valuable guide to the course the furnace was taking. Recently, however, a two-tap system has been introduced, and this guide has been less readily available. Experiments have been conducted in the laboratory in regard to pyrometric control based on the temperatures there, and on a number of chosen indicative condensers. The size, shape and operating temperature of the condensers themselves are also being studied as part of a large investigation into the subject of condensation as it applies to the metallurgy of zinc.

The tapping operation is performed as follows. The liquid metal is withdrawn by small, iron rabbles into large ladles held under the condensers. These ladles, having a capacity of 900 lb., are supported by a system of overhead runways, which have been recently installed and supplant the small hand ladles originally used. After the surface of the metal has been skimmed clean of oxide, the metal is cast into molds. Each plate weighs between 43 and 45 lb. The quality of the metal from the two taps will be referred to later.

LABOR

Much has been said for and against the piece-work system in industry, but in horizontal-retort operation the efficiency of the process is so interlocked with the skill and efficiency of the workmen that it is impossible to differentiate altogether between the metallurgical control and the personal efficiency of the labor force. At Avonmouth this has led to a scheme whereby the workmen are to a large extent partners in the production of spelter and share in a very large measure in its fortunes. Their wage varies with the price of the metal; it depends on the weight they charge into the furnace and also on the over-all zinc recovery, as a reflection of the skill in careful charging. Bonuses are earned also on condenser life and similar occurrences, to encourage careful handling of these

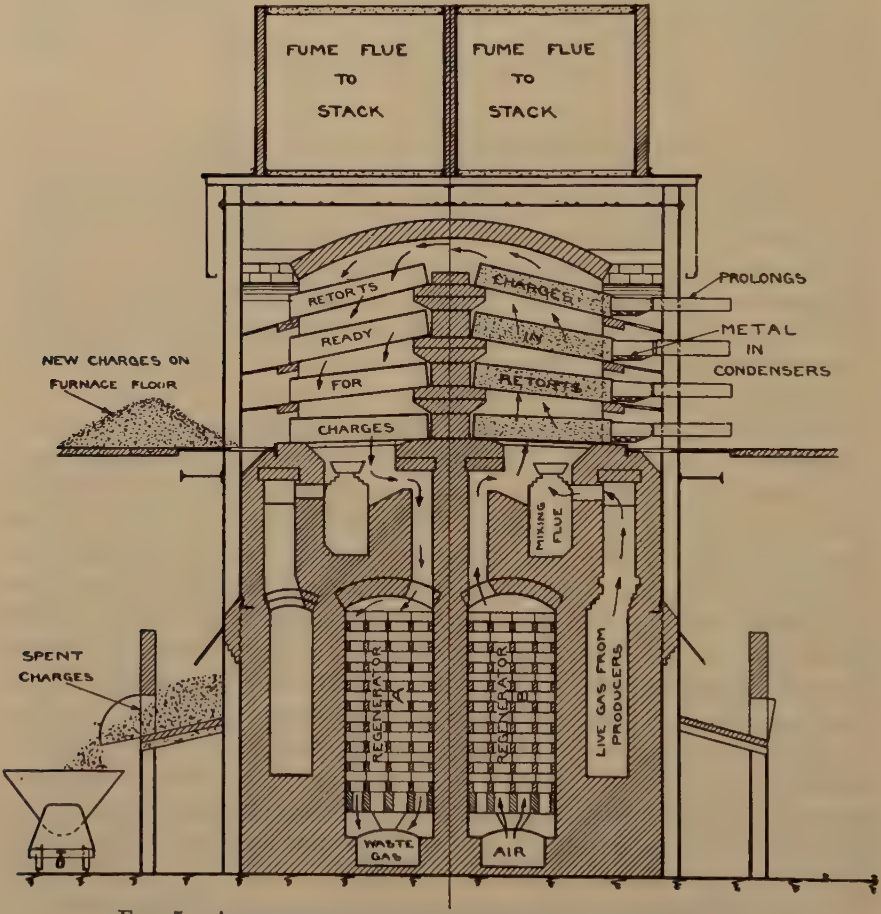


FIG. 5.—AVONMOUTH FURNACE DURING DISTILLATION PERIOD.

articles. This scheme is not without complications when big variations occur in any of the component items, but it has added importantly to the development of the efficiency of the work.

The men are under constant medical surveillance, and every effort is made by the company to keep them fit enough for the arduous work they have to perform. In addition to the mechanically supported ladles, which render the tapping operation less arduous, screens or blinds have been introduced to protect the maneuver gang from the heat of the furnace during stirring out. Fume is withdrawn behind the screens by means of an exhaust system. A cold-air douche system has also been introduced, which delivers cool air through a series of nozzles over the workmen, thus improving the quality, and lowering the temperature, of the atmosphere in which they work.

The statistics of the process in Table 1 are of interest in that they indicate the amounts handled and produced per man.

TABLE 1.—*Horizontal Retort Practice*

Charge:		*Yield:*	
Per furnace, tons	37.44	Per furnace, tons	12.31
Per retort, lb	218.4	Per retort, lb	71.79
Per cu. ft. of retort, lb	85.3	Per cu. ft. of retort, lb	28.04
Per maneuverman, lb	4,193	Per maneuverman, lb	1,378
		Per tapper, lb	12,251
		Per producerman, lb	9,189
		Average per man, lb	1,092
Coal:			
Reducing coal p.t.m., tons			0.74
Gas coal p.t.m., tons			1.89
Total			2.63
Retort life, days	36–40	Condenser life, days	6.5–7.0
Recovery, per cent			89–93

REFINING

The quality of the metal distilled varies during the distillation period, the lead content tending to be higher in the last tap. The iron content also tends to be higher in the last tap, and is due mainly to contamination with the charge itself. The lead, cadmium, and iron content of the spelter vary also in accordance with the constitution of the ores distilled. The two sets of analyses in Table 2 give an indication of the grade of metal in recent first and last taps.

In general, horizontal-retort spelter has been sold in England as G.O.B. (good ordinary brand) and the quality has tended to vary considerably from one consignment to another, particularly in regard to lead content. Over the last 10 years, however, the company has endeavored

TABLE 2.—*Analyses of Recent First and Last Taps*
May 31 to June 31, 1936

Tap	Composition, Per Cent					
	Pb	Fe	Cd	Cu	As	Zn by Difference
First	0.81	0.053	0.046	0.0040	0.0004	99.0866
Second	1.57	0.116	0.021	0.0078	0.0006	98.2846

to establish a good, consistent brand, and this has been achieved by refining larger proportions of the furnace output. The first tap metal is sold direct from the furnaces. The whole of the later tap—about 50 per cent of the output—however, is refined in a special type of liquating furnace, which has been developed on the site. This consists of a large reverberatory type of liquating bath kept at a temperature of approximately 450° C. An overflow from this bath feeds a smaller tapping bath, where the metal is kept at a higher temperature convenient for casting. An analysis of metal produced from this furnace is as follows: Pb, 1.04 per cent; Fe, 0.022; Cd, 0.026; Cu, 0.0054, As, 0.0004; Zn, by difference, 98.9062. The analysis for the average salable production—i.e., this material averaged with the first tap metal—was: Pb, 0.89 per cent; Fe, 0.041; Cd, 0.039; Cu, 0.007; As, 0.0005; Zn, by difference, 99.0225.

CONCLUSION

Although the horizontal process retains much of its original form, ancillary improvements have materially increased its usefulness, but its ultimate continuance must still be in doubt in view of the emergence of other less arduous processes.

New Jersey Zinc Company Vertical Retort Process*

By E. H. Bunce,† Member A.I.M.E., and E. C. Handwerk‡

The inherent difficulties of zinc smelting arise from the fact that metallic zinc is volatilized at the reducing temperature of zinc oxide and thus is liberated in the form of a vapor. This vapor must be subsequently condensed to obtain metallic zinc, first in molten and eventually in solid form. Zinc vapor is sensitive to oxidation not only by air but by combustion gases containing carbon dioxide. It is, therefore, necessary to carry out both the reduction and the condensation operations in a closed system consisting of an externally heated muffle with attached condenser from which external oxidizing agencies are excluded. However, the reoxidation of zinc vapor cannot be entirely prevented by excluding external sources of oxidation. Internal sources of oxidation are necessarily present when oxidic zinc ores are reduced by a carbonaceous reducing agent. The reduction reactions themselves involve, first, the production of carbon monoxide in an amount at least equal in volume to the zinc vapor produced in the reaction, and, second, the formation of carbon dioxide. Not all of the carbon dioxide is reduced again to carbon monoxide by the excess carbon in the time available, and the slightly oxidizing condition, which results, seriously affects the efficiency of the condensation of the zinc vapor to the metallic state.

In the past the difficulties arising from these causes have limited practical zinc smelting on an industrial scale to the use of small retorts equipped with small condensers. The retorts had to be small, because a closed refractory container capable of excluding oxidizing gases from the heating chamber surrounding the retort could not be built in large dimensions. The size was also limited because ordinary refractories when thin enough to conduct heat readily are not capable of sustaining a heavy load of charge at high temperature. Moreover, a loose charge of zinc ore and carbonaceous reducing material such as fine anthracite coal or coke breeze is a poor conductor of heat, thus limiting the cross section of the retort. The operation of these small retorts requires arduous

---

Manuscript received at the office of the Institute Oct. 30, 1936.

* United States Patent Nos.: 1378411, 1678607, 1680726, 1712132, 1749126, 1749127, 1810070, 1811910, 1835460, 1838296, 1863711, 1873861, 1877123, 1896221, 1918245, 1921820, 1929408, 1983025, 1998440, 2009547, 2013980, 2015336, 2021284 2036566, and corresponding patents in many foreign countries.

† General Manager, Technical Department, New Jersey Zinc Co., Palmerton, Pa.

‡ Investigation Engineer, New Jersey Zinc Co.

manual labor and the furnace crews must receive specialized training if efficient results are to be obtained.

The vertical retort process of the New Jersey Zinc Co. has overcome the difficulties mentioned and makes it practicable to smelt zinc ore in continuous operation in large retorts and condense the resulting zinc vapor in large condensers. This has made it possible to substitute mechanical operation for the most arduous and highly specialized manual operations involved in the usual method of zinc smelting.

The problem of increasing the size of the retort has been solved by constructing it of individual bricks and placing it in a vertical position. This has removed most of the weight strain from the walls of the retort and reduced the tendency to cracking under operating conditions. These units have a very large capacity. The selection of refractories and the design of the joints have produced a satisfactory gastight retort. The fact that these units are continuously operated has reduced materially the thermal strains that the older retorts had to withstand.

The condition of the charge has been decidedly changed. Instead of a loose mass of finely divided material, the vertical retort charge consists of denser masses (briquettes) which possess higher heat-transfer factors. This preparation of the charge has materially aided the thermal conditions within the retort by increasing the factors of radiation, convection and conduction.

The difficulty of supplying heat to the charge is met in the first place by the use of refractories of high heat conductivity such as silicon carbide, so that heat can readily pass through the retort wall. In the second place, by forming the charge into agglomerates that retain their form during the smelting operation, voids are provided through which the heat can be transferred from the retort walls to the charge by radiation and convection. This is in addition to conduction, which in the usual method employed in zinc smelting is the most important element in transferring heat to the charge. Moreover, the structure of the individual agglomerates facilitates the conduction of heat from the surface of the individual agglomerate to its core. Thus all three of the methods by which heat can be transferred are efficiently utilized in the process to transfer heat from the retort wall to the charge.

Continuous operation has made it possible to maintain fairly uniform conditions of temperature at the gas and vapor exit of the retort. This means that large condensers can be operated successfully. Some reoxidation of zinc vapor by carbon dioxide does occur before the gases bearing zinc vapor reach the condenser, but the resultant zinc oxide is removed from the gases by the hot coked charge contained in the retort extension between the retort and the condenser, so that this reoxidation product product does not interfere with efficient condensation of the zinc vapor.

A flowsheet of the process is given in Fig. 1.

General Description of Process

The vertical furnace process may be divided into the following steps:

1. Preparing the charge for reduction.
    - *a.* Mixing zinc ore with reducing agents and binders.
    - *b.* Densifying and briquetting the mix.
    - *c.* Drying and coking the briquettes.
2. Reduction of the charge.
3. Condensation of the zinc vapor.

The furnace used to coke the briquettes produced from the mixture of zinc ore, reducing agent and binder is heated by the exhaust combustion gases from the firing chamber that supplies heat to the vertical retort in which the coke briquettes are subsequently reduced. The exhaust gases from the coking furnace are sent to a waste-heat boiler in which steam is generated for supplying part or all of the power required in the plant. The exhaust gases from the waste-heat boiler are then used to dry the moist briquettes from the briquetting press. The thermal efficiency of the process may be better appreciated by tracing the flow of heat. The condenser gases are fired (together with other gaseous fuel) in the firing chamber that heats the vertical retort in which the charge is reduced. Thus part of their heat of combustion is directly utilized for the reduction of the zinc ore. The sensible heat remaining in the exhaust gases discharged from the firing chamber is then utilized not only in conventional recuperators to preheat the combustion air for the firing chamber of the vertical retort, but also to coke the briquetted charge, to produce steam in waste-heat boilers, and finally to dry the crude briquettes. Further

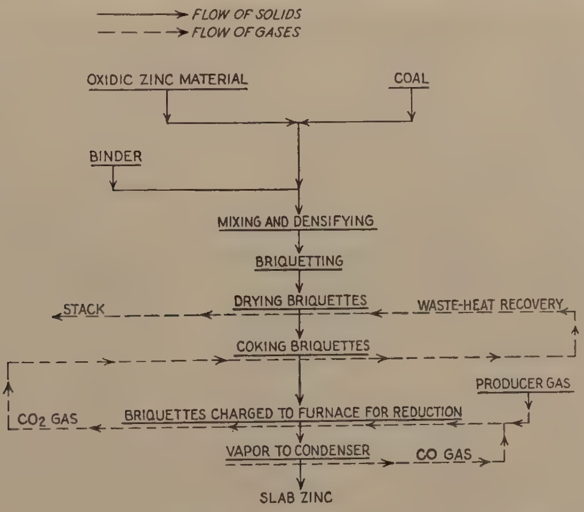


Fig. 1.—Flowsheet of vertical retort process.

heat economy is brought about by charging the coked briquettes from the coking furnaces into the vertical retort while still hot and by preheating the fresh batch of charge by heat interchange with the reduction gases from the retort, which traverse the charging extension of the retort on their way to the condenser.

Preparing Charge for Reduction

Mixing

As indicated above, one vital feature of the process consists in the use of a charge that can be readily heated. It is also essential that the charge be capable of flowing readily through a vertical retort by gravity without bridging or sticking. These prerequisites are secured by the production of coked agglomerates of zinc ore and reducing fuel that retain their form and shape throughout the reducing operation; that is to say, do not break down into fines when their zinc content has been thoroughly eliminated by the smelting operation. The following procedure has been successfully adopted for the preparation of a charge satisfying these requirements:

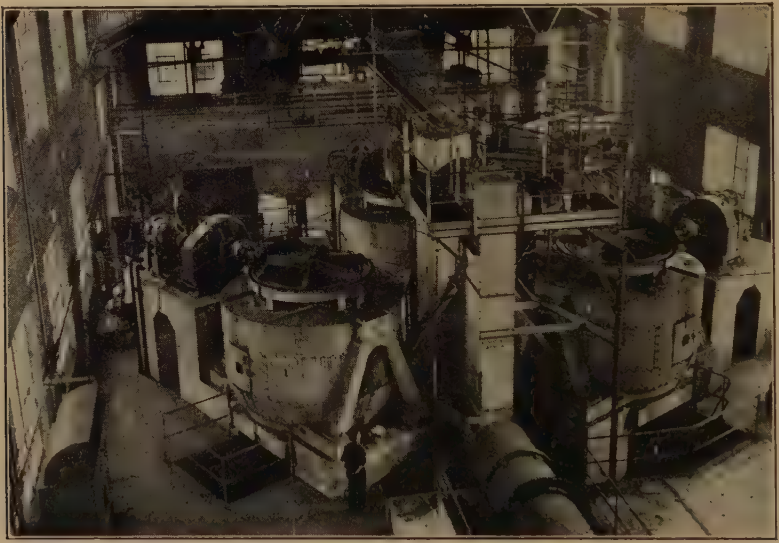


Fig. 2.—Battery of Chilean mills.

The oxidic zinc ore to be treated is first mixed with carbonaceous reducing material consisting at least in part of coking coal; for example, a mixture of fine coking coal and anthracite in various proportions may be used, the amount of coking coal used being adequate to obtain a continuous structure of solid coke throughout each individual briquette during the subsequent coking operation. The ingredients of the charge are first mixed in a mixing device, for example, a rotary cement mixer. The mixture is then thoroughly kneaded by treatment in edge runners or Chilean mills (Fig. 2) operated in series. A binder such as sulphite waste liquor, tar, pitch or molasses is added to the charge during its treatment in the edge runners. This binder is essentially a temporary binder, being required only to enable the briquettes to retain their shape without disintegration during the operations of discharging them from the briquetting press, transferring them to the coking furnace and coking them therein. A thorough mixture of the charge ingredients and densification of the mix are essential.

An appropriate amount of water is introduced into the finished mix in a paddle mixer, which discharges the moistened charge material to a densifying press. The densifying press is a roll briquette press, which discharges small briquettes to the final briquetting press, likewise a roll press. The wet briquettes discharged from the final briquetting press are then dried by bringing them into contact with the exhaust gases from the waste-heat boilers (though sometimes this drying operation may be omitted). The briquettes are then ready for transfer to the coking furnaces.

Coking

The coking operation is carried out in a vertical chamber of rectangular cross section through which the briquettes continuously pass. The heating is effected by direct contact between the briquettes and the exhaust gases from the firing chamber used to heat the vertical reduction retorts. The long walls of the vertical coking chamber are provided with louvers or slots, so that the hot exhaust gases can be passed through the coking chamber in a horizontal direction while the briquettes to be coked descend by gravity. The heating gases enter the coking chamber at a temperature from 750° to 900° C. They leave the coking chamber at 300° to 700° C. If the briquettes have had preliminary drying the exit temperature of the gases will ordinarily be substantially above the minimum figure named.

In consequence of the direct contact with the heating gases, the briquettes are rapidly coked. The coking furnace is operated intermittently, fresh briquettes being charged into the top (Fig. 3) while coked briquettes are removed from the bottom by means of a roll discharge. The hot coked briquettes are discharged (Fig. 4) from the coker (over a grizzly that screens out any fines) into buckets; these buckets are raised to the charging hoppers of the vertical retorts and the briquettes are charged into the vertical retort while still red hot. The fines that pass through the grizzly are returned to the mixing operation for re-use in compounding the charge.

The production of good coked briquettes requires not only a thorough mixing and densifying of the charge before briquetting but also an appropriate selection of coking coal and careful control of the degree of preliminary crushing of the coals and ores prior to the mixing.

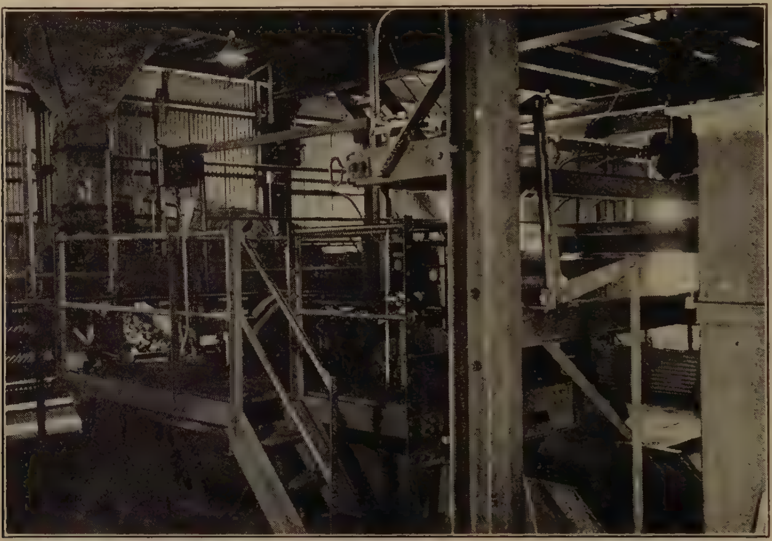


FIG. 3.—BRIQUETTE PRESS ON PLATFORM AT LEFT, AND ACCUMULATOR CAR FEEDING BRIQUETTES TO COKING FURNACE.

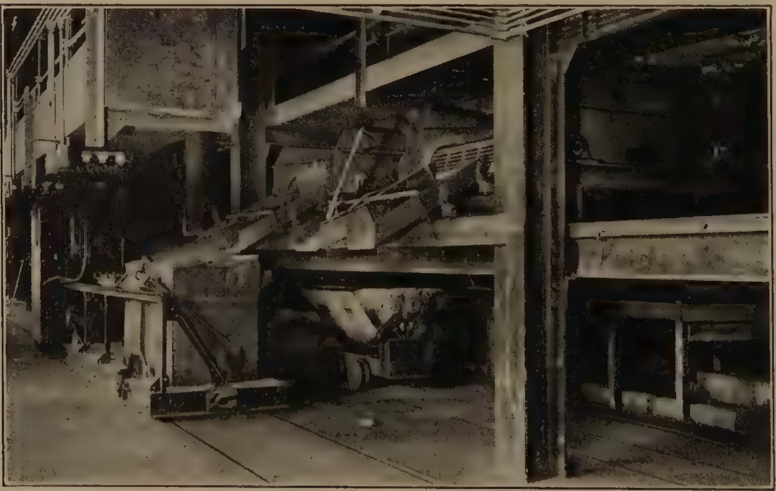


FIG. 4.—GENERAL VIEW OF DISCHARGE AT COKING FURNACES SHOWING LARRY FOR COKED BRIQUETTES.

The exhaust gases from the coking furnace are sent through a flue to the waste-heat boilers. Air is admitted just ahead of the waste-heat boilers in order to insure the combustion of the combustible constituents (mostly hydrocarbons expelled from the briquettes during the coking operation).

REDUCTION

The following details are added to supplement the general description of the reduction retorts given in the introduction. The retort is vertical and of rectangular cross section (Fig. 5). Its heated height is ordinarily 25 ft. The internal width of the retort is 1 ft. The length of the cross section (measured internally) varies; the usual length is now 6 ft., but the original retorts were 5 ft. long and retorts 7 ft. long are in successful operation. The long walls of the retort fit into slots in the end walls, these slots being provided with glands filled with granular silicon carbide and graphite. These slots thus form a slip joint that is impermeable to zinc vapor, which permits the walls to expand and contract independently, a factor that greatly decreases the mechanical strain on the retort. The retort is extended at both the top and the bottom (Fig. 6). The upper extension is constructed of refractories, and is kept filled with fresh charge

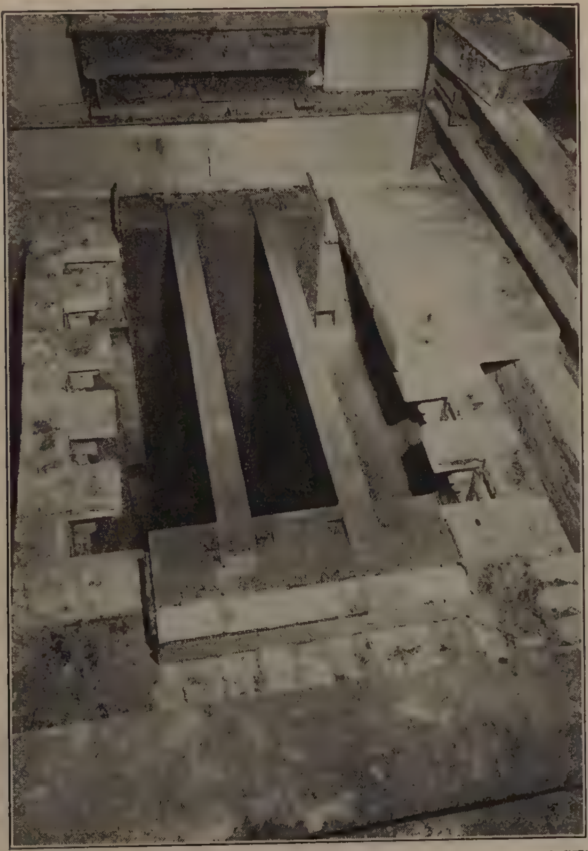


FIG. 5.—PARTLY COMPLETED VERTICAL RETORT IN FURNACE SETTING.

about to undergo reduction. The lower extension of the retort leads down into a water seal. This extension as well as the water seal are ordinarily constructed of sheet iron.

The retorts are operated continuously, but the charge is introduced in batches (Fig. 7) at intervals long enough to permit the formation, by reason of the continuous discharge at the bottom, of adequate space in the top extension to accommodate the fresh batch of charge.

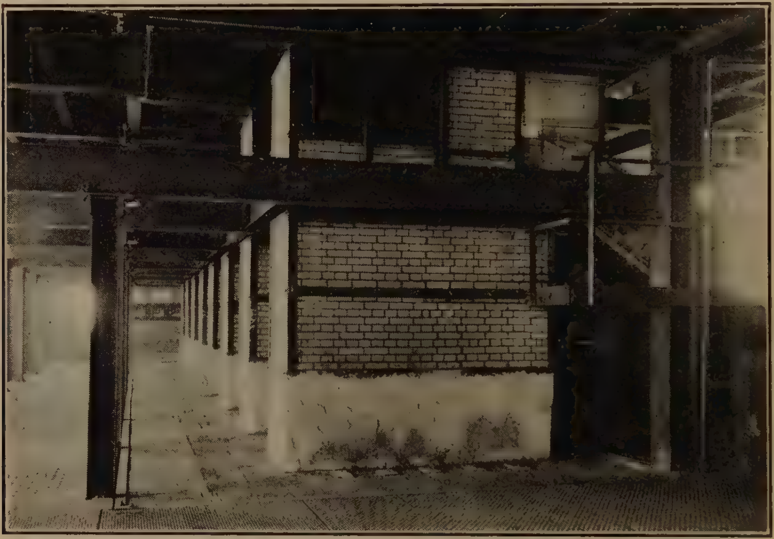


Fig. 6.—Side and rear view of upper extensions of the retorts.

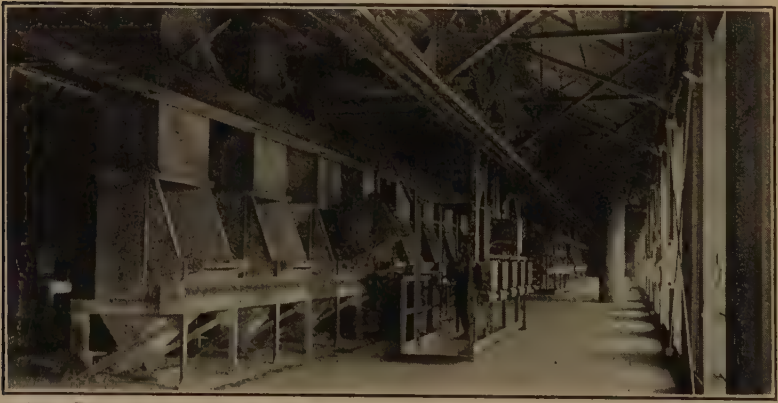


Fig. 7.—Charge floor showing electric-hoist charge larry in operation.

Heat is introduced into the retort by a combustion chamber opposite each long wall. The distribution of gas and air in the firing chambers is so arranged as to secure uniform heating over the entire wall. As mentioned in the introduction, the transfer of heat from the hot retort wall to the charge is greatly facilitated by the agglomerated nature of the charge. Radiation, convection and conduction are all utilized efficiently in supplying heat. Since the reduction of zinc oxide by carbonaceous reducing agents is an endothermic reaction, the rate of reduction and thus the producing capacity of the retort is governed by the amount of heat that can be introduced into the charge. Aside from the factors already mentioned, the good heat conductivity of silicon carbide greatly facilitates the supply of heat to the charge.

Displacement gas consisting of air or exhaust combustion gases is introduced under appropriate pressure at the base of the charge. This displacement gas maintains an upward flow of gases and vapors through the retort. This upward flow carries the zinc vapors evolved from the charge during the reduction towards the condenser and thereby prevents the condensation of zinc vapor upon the cooling residue in the lower extension of the retort. Such condensation of zinc vapor would result in the loss of zinc in the form of shot metal in the residue. Any oxidizing constituents such as oxygen or carbon dioxide that may be present in the displacement gases are transformed to carbon monoxide by reaction with carbon in the charge during the passage of the gases through the retort, so that no oxidation of zinc is brought about by the displacement gas. An alternative method of operating the retort is to use an open bottom and regulate the flow of gases to the condenser by stack-draft control.

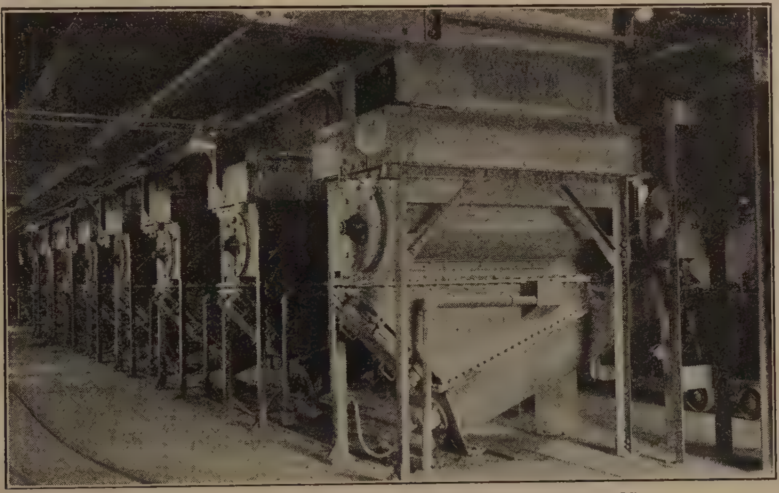


FIG. 8.—GENERAL VIEW OF RESIDUE DISCHARGES.

The spent briquettes are continuously discharged from the retort by an automatic roll-discharge mechanism into a water seal. The briquettes do not disintegrate during the reduction operation, but are discharged from the retort in substantially their original shape and size. The lower metal extension of the retort cools the residue briquettes sufficiently to allow them to be received in the water seal without the evolution of enough steam to interfere with the operation of the retort. The quenched briquettes are finally removed from the water seal by a simple screw conveyor (Fig. 8). The metals contained in these briquettes, such as lead, copper and precious metals that may have been present in the zinc ore, as well as their excess carbon, may be recovered and utilized by a number of known and conventional metallurgical operations.

The three chief variables that control the output of the retort are the size of the retort, the temperature at which it is fired and the condition of the charge. Experience has shown that an average output of 30 lb. of metallic zinc per day of 24 hr. with 96 per cent elimination and 92 per cent recovery can be obtained for each square foot of heated long wall surface by firing at 1300° C., provided the coked briquettes used are of good quality and yield a good firm undisintegrated residue. Instruments for recording temperatures of furnace chambers are shown in Fig. 9.

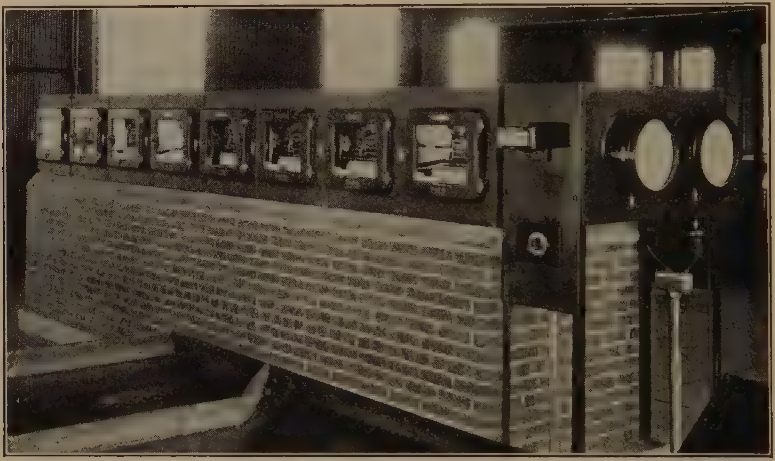


Fig. 9.—Instruments recording furnace-chamber temperatures.

Condensation

The condensation of metallic zinc from the zinc vapor is greatly facilitated in the vertical retort process by the fact that a continuous supply of large volumes of gases carrying zinc vapor, gases of constant composition and at constant temperature, are produced. This renders it possible to operate large condensers under substantially uniform conditions; as a consequence those conditions of condenser temperature and pressure that have been found favorable can be continuously maintained.

However, certain inherent difficulties in the condensation of zinc vapor have had to be overcome in the vertical retort process. A more detailed consideration of these difficulties requires a brief statement of the chemical reactions occurring in the reduction of oxidic zinc ores by carbonaceous reducing agents. The reduction reaction is probably initiated by the reaction of solid carbon with zinc oxide:

$$ZnO + C = Zn + CO \qquad [1]$$

The carbon monoxide thus formed (and, in the vertical retort process, the carbon monoxide formed by the reaction of the oxidizing constituents of the displacement gas with the carbon in the charge) then reduces further zinc oxide in accordance with the following reaction:

$$ZnO + CO = Zn + CO_2 \qquad [2]$$

The carbon dioxide thus formed tends at temperatures above 900° C. such as prevail in the zinc-producing retort to react with carbon to form carbon monoxide:

$$C + CO_2 = 2CO \qquad [3]$$

so that zinc vapor is not reoxidized at such temperatures. This is the familiar gas-producer reaction. However, this reaction tends to be too slow to remove all the CO_2 from the gases before they have left the heated zone of the reduction retort. In the vertical retort process, the reduction of carbon dioxide is substantially completed in the upper extension of the retort, by the reaction of residual carbon dioxide in the gases with the hot coked briquettes or with the zinc vapor. These briquettes likewise filter zinc oxide and entrained particles of charge from the gases. Another possible source of CO_2 is the reversal of the gas-producer reaction:

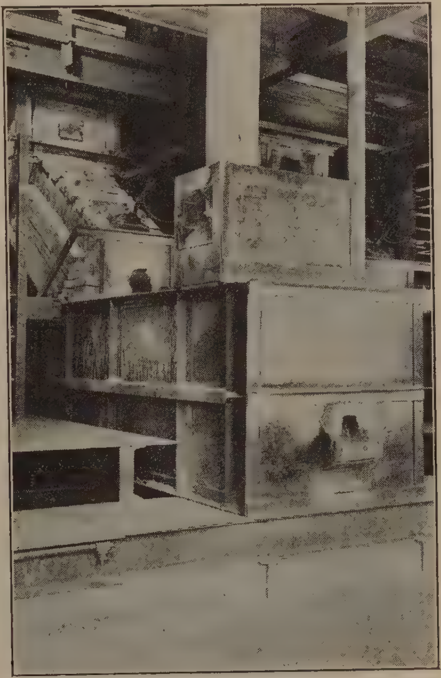


FIG. 10.—CONDENSER.

$$2CO = CO_2 + C \qquad [4]$$

To whatever extent this reaction takes place it increases the amount of chemical blue powder formed. The blue powder so formed on the descending charge is automatically returned to the reduction zone of the retort.

The condenser (Fig. 10) consists of two parts, which are operated under different thermal conditions. The first part of the condenser is an inclined conduit directly connected to the zinc-vapor orifice of the retort.

This conduit is so designed that the gases therein are rapidly cooled. The second portion of the condenser consists of a sump in which the molten metal is collected and in which the cooling and condensation of the zinc vapor are completed at a relatively slow rate in order to avoid the formation of substantial amounts of physical blue powder by excessively rapid chilling of the zinc vapor at this stage. The formation of physical blue powder in consequence of the entrainment of zinc oxide and ore dust from the retort charge is likewise greatly decreased by the filtering action of the charge in the upper extension of the retort.

Both the descending conduit of the condenser and the condenser sump are equipped with baffles set sideways to bring about a zigzag and turbulent flow of the vapors through the condenser. The baffles used are of silicon carbide and are so set in the condenser that they can be utilized if desired as radiating fins to intensify and regulate the cooling of the condenser where necessary. Thus the baffles may be pulled out somewhat so as to project further, in order to intensify the loss of heat from the condenser by radiation. Further thermal control in the direction of decreasing the radiation of heat from the condensers may be secured by insulating either the descending conduit or the condenser sump when this is desirable.

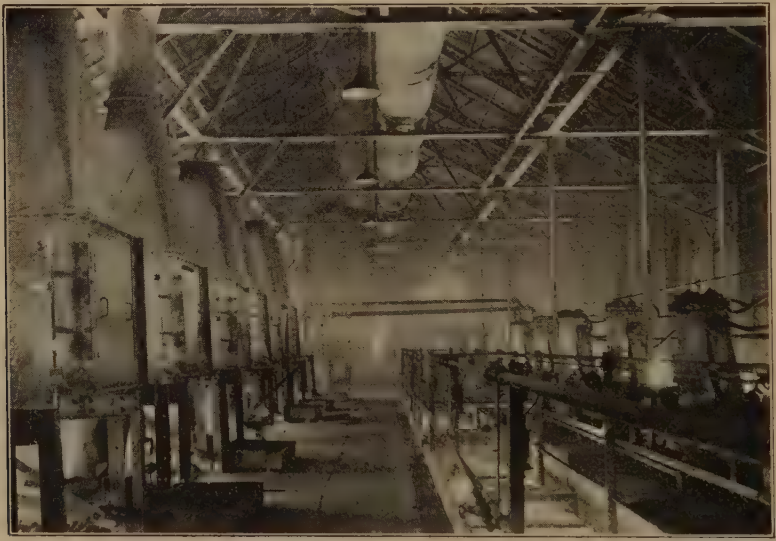


FIG. 11.—REAR VIEW OF CHARGE HOPPERS (ON LEFT) AND CONDENSER OUTLETS, SHOWING SCRUBBERS.

The exhaust gases from the condenser are discharged through a stack into a scrubber (Fig. 11) operated with a water jet and Venturi tube eductor in such a fashion as to withdraw the exhaust gases from the condenser by suction. The pressure prevailing in the condenser can be regulated thereby. The scrubber removes the last remnants of zinc vapor from the condenser exhaust gases. This residual zinc is collected from the scrubbing water in the form of zinc dust, by sedimentation. The cleaned condenser exhaust gases, consisting to a great extent of carbon monoxide, are then sent to the combustion chamber that fires the retort. Under ordinary operating conditions these condenser exhaust gases supply 20 per cent of the heat needed to fire the retort, so that substantial economies with regard to heating fuel are brought about thereby. The condenser exhaust gases are richer in fuel value than ordinary producer gas so that no difficulties are encountered in burning them to advantage.

The molten metal is tapped from the condenser sump into ladles (Fig. 12) at appropriate intervals and cast into slabs. The zinc dust from the condenser, together with the zinc dust recovered in the scrubber, may be either directly recharged into the retort or marketed. The circulating load of zinc thus established in the vertical retort is about 8 per cent of the zinc charged.

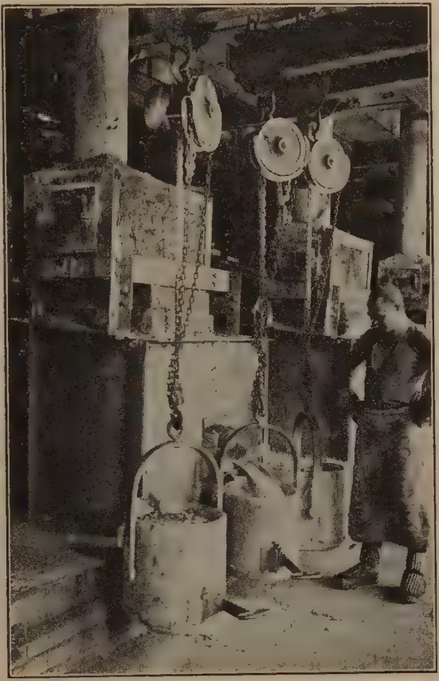


FIG. 12.—TAPPING CONDENSER.

GENERAL ADVANTAGES OF THE PROCESS

The New Jersey Zinc Co. vertical retort process has achieved a thoroughgoing mechanization of the pyrometallurgical reduction of zinc. Thus manual labor has been substantially eliminated from the hitherto arduous operations of charging and discharging the retorts. Moreover, the time-consuming operation of collecting small batches of molten zinc in great numbers in small condensers has been replaced by the simple step of tapping zinc in large amounts (about 1¼ tons) from a large sump into ladles. This achievement has improved working conditions and increased the output to one ton of metal per man-day.

The zinc recovery is high in the vertical retort process, since the losses are chiefly confined to those incurred in handling the ore (dusting, spillage and the like) and to the small percentage of zinc remaining in the residue. The elimination of zinc is excellent. The recirculating zinc load (consisting of recharged zinc dust from the condenser and scrubbers) is small.

The thermal efficiency of the process is high on account of its continuous character, the use of large retorts with resulting decrease in heat loss, the efficiency of transfer of heat to the charge, the recovery of the high latent heat values in the gas discharged from the condensers and the utilization of the products of combustion from the firing chamber heating the vertical retorts not only to preheat the combustion air but also to dry, coke and preheat the charge itself and to produce power by the use of waste-heat boilers, thus recovering a large portion of heat in the exhaust stack gases.

Long retort life is secured by the rugged construction and uniform operating conditions prevailing in the vertical retort plant. A normal retort life is from three to five years or more.

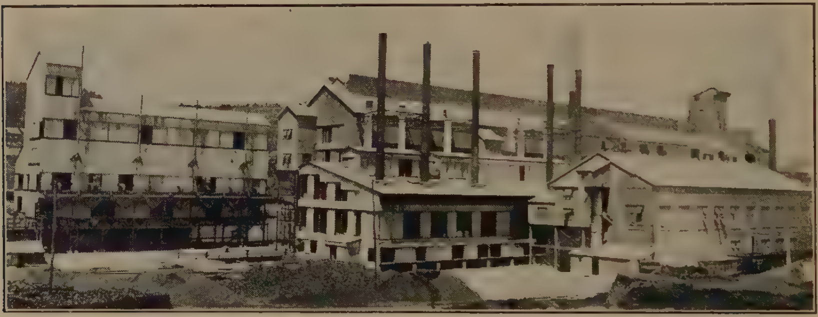


Fig. 13.—General view of vertical retort plant at Palmerton, Pa. Left to right: gas house, furnace building and mix house.

Commercial Application

The first commercial vertical retort plant was constructed by The New Jersey Zinc Co. (of Pa.), at Palmerton, Pa. (Fig. 13), and placed in operation in May, 1929. This plant has been in successful operation since that time. Originally the plant contained 16 retorts, and 12 more retorts were placed in operation in 1936, bringing the total vertical retort capacity at Palmerton to 28 retorts. A vertical retort plant comprising 8 retorts was placed in operation by The Mineral Point Zinc Co. (a subsidiary of The New Jersey Zinc Co.) at Depue, Ill., in July, 1929. The Grasselli Chemical Co. built a 16-retort plant at its Meadowbrook plant at Spelter, West Va., in 1930, and this plant has been in successful operation since August of that year. The National Smelting Co., Ltd., through its subsidiary, Improved Metallurgy, Ltd., completed a plant at Avonmouth, England, comprising 16 vertical retorts, and placed it in operation in August, 1934. The Unterharzer Berg- und Hüttenwerke, G.m.b.H., is now constructing a plant comprising 8 retorts, at Oker, in the Harz Mountains, Germany. It is expected that this plant will be placed in operation in December, 1936, and plans are now being prepared for its extension.

Manufacture of Silicon Carbide Retorts

By E. J. Bruderlin,* Member A.I.M.E.

A metallurgical process to be economically successful must be carried on under proper conditions of control and equipment. The question of equipment is always of primary importance. In the distillation process for the recovery of zinc by retorting, the retort is the all-important piece of equipment. Each retort in a working block must function as a separate unit. Over-all block efficiency is the result of the ability of the individual retort to withstand the severe conditions of operation for a maximum period of time. Therefore retort manufacture has been an ever present problem with the operator of a zinc-retorting plant.

During recent years the zinc-plant operator has been faced with rapid changes in the character of the ores and concentrates. Operating costs have increased as a result of the introduction of the flotation process and the amount of flotation concentrates to be handled. To counteract increasing costs, the operator has found it necessary continually to attempt heavier loading of retorts, until a 45 to 50-lb. charge per cubic foot of retort space has become common practice. Heavy loading has brought about severe firing conditions, which, in turn, have emphasized the necessity for further improving the quality of the retort. Increasing percentages of detrimental impurities in the retort charges have also added to the operator's difficulties.

AMARILLO SILICON CARBIDE RETORTS

At the Amarillo plant of the American Smelting and Refining Co. a retort made of a suitable plastic clay grogged with silicon carbide has been found to best meet the present-day requirements. Retorts of this kind have been in use at Amarillo for 8 years and have shown an average furnace life of approximately 175 calendar days.

The Amarillo retort is cylindrical in shape and after burning is approximately 8¾ in. inside diameter by 60 in. over-all length. The wall thickness is 1⅛ in., except for the butt of the retort, which is approximately 2½ in. thick. The retort mud has a shrinkage of 3 per cent, or approximately ⅜ in. per foot. The silicon carbide retort after being properly dried weighs about 211 lb. When the retort is fired and ready to go into use the weight decreases to approximately 203 lb.

Manuscript received at the office of the Institute June 1, 1936.

* American Smelting & Refining Co., Amarillo, Texas.

Clay Used.—Suitable plastic clay for the Amarillo silicon carbide retorts has been obtained from several sources. At first, a St. Louis plastic clay mined at the now abandoned Williams mine, in the Cheltenham district, was used. This clay was particularly suited for retort work because little weathering of the raw clay was necessary. The nature of a zinc-retorting operation, especially one in the natural-gas field, makes impossible the use of a clay that requires long periods of weathering. All operators will agree that a zinc-retorting operation should not be limited or delayed by processes that require long periods of time, such as the weathering process required for making clays workable. Plastic clay obtainable from the Stone City district of Colorado is now being used successfully at Amarillo.

Typical analyses of the raw plastic clays are given in Table 1. Seger cone tests on both types of clay show a softening point at cone 31.

TABLE 1.—*Typical Analyses of Clays Used for Amarillo Retorts*

	Cheltenham (Williams Mine), Per Cent	Colorado (Stone City), Per Cent
Loss on ignition	9.7	12.0
Silica	62.8	58.4
Alumina	21.8	24.2
Ferric oxide	2.2	2.6
Titania	1.4	0.8
Lime	0.35	0.55
Magnesia	0.29	0.65
Alkalis	0.31	0.36
Sulphur	0.48	0.18

The moderately weathered clay is prepared for mixing by first crushing in a jaw crusher and standard rolls to the point where all will pass through a screen of 7 × 7 mesh and 0.072-in. diameter wire.

Mixing Clay and Carbide.—The mixing of the plastic clay and the silicon carbide in the proportions of 65 parts of silicon carbide and 35 parts of plastic clay by weight is carried on in a Clearfield Machine Co. 6-ft. wet pan. The crushed clay is carefully weighed and placed in the pan, where it is ground for several minutes. The silicon carbide is then added and the mixing continued for 12 min. Water is added from time to time during the operation. As little grinding as possible is permitted at this point, so as to avoid the breaking down of the silicon carbide grain. A typical batch mix consists of 126 lb. of clay, 234 lb. of silicon carbide and about 35 lb. of water.

The silicon carbide used at Amarillo at present is produced by the Carborundum Company of Niagara Falls, N.Y. It is described as first-grade, crystalline, refractory silicon carbide and designated as

No. 1 pan milled "type C crushing" silicon carbide, with an approximate screen analysis of grain as follows: 14 to 36 mesh, 55 ± 5 per cent; 40 to 70 mesh, 25 ± 5 per cent; 80 and finer, 20 per cent ± 5 per cent. This analysis is determined by a 5-min. test of a 100-gram sample on a Ro-tap with A.S.T.M. screens.

The impurities in the silicon carbide are principally free carbon, free silica, iron, lime and alumina. The total combined silicon and carbon should exceed 96.5 per cent. A typical analysis is as follows: combined carbon, 28.4 per cent; combined silicon, 67.1; Fe, 0.8; MgO, 0.0; CaO, 0.37; Al, 1.2; free carbon, 0.2; free silica, 1.9. Recent experiments have indicated that a smaller proportion of bonding clay may prove advantageous.

Preparing Mud.—The retort mud, after being mixed and prepared in the wet pan, is handled by means of wheelbarrows from the wet pan to a Stearns-Rogers pugmill. It is allowed to accumulate on the floor near the pugmill until sufficient mud is present to permit proper operation of the mill. The first step consists of pugging the mud into cylindrical shaped balls 13½ in. in diameter by 9 in. long, which are delivered to the rotting rooms and there placed in regular piles and covered with wet burlap. During the rotting period, which continues for at least 10 days, the retort mud is repugged at least twice, to produce the finished retort mud.

Just before the delivery to the retort press, the finished retort mud is again repugged and cut into balls 13½ in. in diameter by 18½ in. long, weighing approximately 245 lb. each. The balls are carefully transferred to the retort press, placed in position in the press, which has been cleaned of all mud from the previous pressing operation, and then extruded at a pressure of approximately 3500 lb. as indicated by the pressure gauge at the hydraulic pump. The correct length is maintained by cutting each retort to a template.

Forming Retorts.—The Amarillo retort press is of the Mahler type, as formerly manufactured by the United Iron Works. Some modifications were necessary to adapt the press to the handling of the stiff silicon carbide mud. The abrasive effect of the silicon carbide is extreme and repairs and replacements are necessarily numerous. Cast-iron matrix bushings and cast-iron heads have been replaced by cast-steel parts. Provisions have also been made to expel as much of the trapped air as possible. The silicon carbide mud, being much stiffer and denser than standard clay muds, requires high pressures in forming retorts.

Silicon carbide retorts are difficult to produce without some wall lamination, but this defect has been greatly reduced at Amarillo by careful control of the moisture content of the retort mud and the elimination of trapped air in the pressing and forming operations.

Drying Retorts.—After being delivered from the Mahler press, the retorts are handled by means of a rubber-tired carrier and placed in the drying rooms, where they are carefully dried for at least 30 days. On account of local weather conditions at Amarillo, much of the drying is done by natural means. Only during a short period of the year is it necessary to provide steam heat in the drying rooms. Since very slow drying is essential, a burlap covering is placed over the retorts and a layer of paper is placed on the floor of the drying room. The burlap covering is moistened frequently by means of a sprinkler, so as to delay the drying of the open end of the retort. During periods of cold weather, when drying rooms are heated with steam, great care must be exercised to maintain uniformly slow drying.

Firing.—The thoroughly dried retorts are transferred from the pottery to the furnaces. There they are placed in the preheating kilns and fired for 48 hr. Since a silicon carbide retort is very sensitive to heat shock, it has been found advisable to increase the temperature gradient during the firing at a rate not to exceed 30° C. per hour, until a maximum temperature of 900° C. has been reached. A recording pyrometer is used, so that the operator may control the firing within close limits. No special effort is made to maintain either reducing or oxidizing conditions within the kiln during the firing but it has been recognized that a strong oxidizing flame has a tendency to blister and damage the retort. The delivery of the silicon carbide retorts from the kiln to the retort block should be made as rapidly as possible, so as to avoid unnecessary cooling shocks.

Retorts in Use.—The manipulation of the furnace temperatures after the retort is placed in position in the retort block is not included in this paper. However, all will agree that proper care and experience are necessary to obtain best results.

New Jersey Zinc Company
Process for the Refining of Zinc by Redistillation*

By W. M. Peirce† and R. K. Waring,‡ Members A.I.M.E.

Zinc of high purity offers definite advantages in certain fields. A process by which zinc of 99.99+ per cent purity is produced by pyrometallurgical methods is described in this paper. The process consists of a fractional distillation following the primary reduction; this fractional distillation employs the principles of rectification for the separation of lead and other high-boiling impurities and cadmium and other low-boiling impurities.

Theoretical Considerations Involved in Production of High-purity Zinc by Distillation

Fractional distillation, fractional condensation, and rectification are recognized methods of separating mixtures of liquids. In the field of organic liquids these methods are widely used but not commonly to effect as complete a separation of liquids as is done in the problem under consideration. Zinc boils at 905° C., cadmium at 778° C. and lead at about 1620° C. Zinc may contain from several hundredths of one per cent to over one per cent each of cadmium and lead, and the problem is to reduce these impurities to a few thousandths of one per cent. For lead and zinc, the spread in boiling points is substantial, 715° C., while for zinc and cadmium it is only 127° C.

The basic limitation of any separation by distillation may be found from the relation between the equilibrium composition of the vapor and the liquid for all mixtures of the two substances involved. If a mixture of constant boiling point is found, or if a stable compound that vaporizes without dissociation occurs, there is a definite theoretical limit to the degree of separation that is possible when operating at atmospheric pressure with respect to that mixture. Otherwise, any degree of separation is theoretically possible.

The equilibrium composition of vapor in contact with liquid mixtures of zinc and cadmium at the boiling point has been determined experi-

---

Manuscript received at the office of the Institute Oct. 23, 1936.

* United States Patents Nos. 1980480, 1994345, 1994346, 1994347, 1994348, 1994349, 1994350, 1994351, 1994352, 1994353, 1994354, 1994355, 1994356, 1994357, 1994358.

† Chief, Metal Research Division, New Jersy Zinc Co., Palmerton, Pa.

‡ Chief, Fundamental Metallurgical Section—Metal, New Jersey Zinc Co.

mentally over the entire range of mixtures from pure zinc to pure cadmium. These data proved that it was possible to obtain any desired degree of separation of zinc and cadmium by distillation. Similar data were obtained for zinc-lead mixtures containing up to an amount of lead above which it is more advantageous to separate lead by liquation. The data showed that zinc of any desired degree of freedom from lead could be obtained.

One step of simple fractional distillation or condensation applied to a given initial mixture can result in only a definitely limited degree of separation. If the mixture is passed through a series of such steps, a substantial degree of purification of the base constituent can be attained, but only at the expense of a considerable loss of the base constituent by inclusion in the separated fractions. Such a method has been used for a long time to produce an improved grade of zinc, but it would not be an economical one for the production of 99.99+ per cent zinc, as too many stages would be required.

For the purification of zinc, rectification, which is a means of integrating in one operation multiple stages of fractional distillation and fractional condensation, may be effectively employed. The liquid metal and metallic vapor travel countercurrently through a column, the heat for boiling being supplied at the lower end of the column, and the heat of condensation removed at the upper end.

The rectification column may be composed of a stack of trays, the liquid metal cascading down through the series of trays and the metallic vapor passing up in intimate contact with the descending liquid metal. Calculations of the possible performance of rectification columns are conveniently carried out in terms of theoretical trays—a theoretical tray being one in which the liquid and vapor reach equilibrium.

It is possible, if the complete relation between the equilibrium composition of vapor and liquid for the mixture being dealt with is known, to calculate the relationships between the several variables involved in the design and operation of a rectification column; namely, the number of trays, amount of liquid boiled at the bottom and condensed at the top (the reflux), the composition of the feed, the point of entrance of the feed to the column, and the purity of both the high-boiling fraction removed at the bottom and the low-boiling fraction removed at the top. The operation may be calculated for either liquid or vapor feed. Such calculations must be supplemented and have been supplemented by practical experiments to determine the size of column of a given design that is equivalent to a given number of theoretical trays. Once determined, this has made possible reasonably accurate prediction of the behavior of other columns of similar design but which vary in size or to which the feed is of different composition or from which different products are required. There can be calculated also the relative economy attain-able by the use of columns of varying lengths and by variation of the supply of heat to the rectification column.

Practical Application

A boiler that will efficiently vaporize zinc at a rapid rate is essential to supply vapor to a column for rectifying zinc. The boiler must be constructed of a refractory material having good heat conductivity, such as silicon carbide. The ordinary boiler problem of presenting maximum surface to hot gases on one side and liquid on the other is here complicated by the necessity of using a refractory instead of metal and the consequent necessity of constructing the boiler of a number of relatively small parts of simple form. These considerations necessitate working with comparatively low hydrostatic heads of liquid metal; that is to say, with shallow baths of liquid.

Practically, the problem has been solved by constructing the boiler of a series of superposed rectangular trays of as large horizontal cross section as the art of refractory manufacture permits, but with a depth of only a few inches. The depth of metal in each tray is regulated by an overflow through an opening in its bottom to the tray below. The openings are staggered so that the overflow from each tray will be caught on the one beneath. There must be an adequate space between the surface of the bath of liquid metal and the bottom of the tray above for the passage of vapor upward through the column without the creation of undue pressure. In order to obtain contact of the maximum possible proportion of the heated walls with liquid zinc, and at the same time provide adequate space for vapor passage, the central part of the tray bottom is raised. The liquid metal is thus contained in a trough extending around the periphery of the tray. This design facilitates heat transfer and increases the boiling capacity of the tray. The trays are preferably monolithic, and as the only joints in such type of construction are the horizontal ones between trays, located above the level of the bath in each tray, no joint is exposed to a hydrostatic head of liquid metal.

In the rectifying column proper, intimate contact between the liquid metal and the metallic vapors is brought about. The column is very similar in design to the boiler; that is, a column composed of a series of superposed trays with staggered openings which permit the liquid metal to cascade downwards in a tortuous path in intimate contact with metallic vapors ascending countercurrently. The depth of liquid metal in each tray is kept to a minimum since a maximum exposed surface and a minimum volume facilitate the attainment of equilibrium. Furthermore, the resulting reduction in area of the surface of contact of the metal with the outside wall helps to minimize heat losses in the rectifying column. The rectifying column is usually of the same horizontal cross section as the boiler and superimposed upon it.

If the zinc to be purified contains relatively high percentages of impurities, a large amount of refluxing may be required for their removal; in such case, a separate condenser at the top of the rectifying column may be required. Otherwise, sufficient refluxing may be obtained by the condensation that occurs in the rectifying trays themselves due to ordinary heat losses. Also, variation in the content of impurities can be met by appropriate changes in the number of trays.

The conventional packed type and bubble-tray type of fractionating columns used for rectifying organic liquids are poorly adapted to the rectification of zinc. The density of liquid zinc is a disadvantage in the bubble-tray type on account of the great resistance to the flow of vapor through the column. The distribution of liquid zinc in packed columns is uneven, owing to the difficulty of wetting most refractory packing materials with zinc, and the tendency of the zinc to condense on the walls of the column on account of the high temperature prevailing in its center. Uneven distribution of zinc over the cross section of the column results in failure to attain sufficiently intimate contact between the liquid metal and the metallic vapor for efficient rectification.

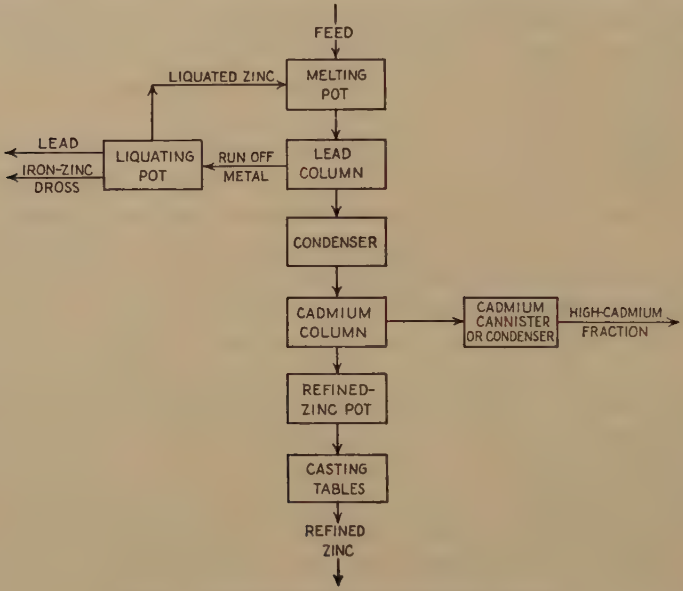


FIG. 1.—FLOWSHEET OF ZINC DISTILLATION.

The dimensions of the boiler and condenser sections of the column are mutually adjusted so that the necessary amount of liquid metal is vaporized at the bottom and the proper proportion of the vapor condensed and refluxed at the top.

The vapor withdrawn at the top of the column, that is, the part of the vapor not condensed and refluxed in the column, is collected in a condenser made of refractory material.

Molten-metal seals at all points where metal is introduced or withdrawn from the system are requisite to prevent escape of zinc vapor or ingress of air.

Heat is supplied to the units by setting them in suitable combustion chambers which may conveniently be gas-fired.

Fig. 1 shows a diagrammatic flowsheet and Fig. 2 a schematic flowsheet, for a typical complete installation. Crude metal is charged to a melting pot that has a melting capacity adequate to supply a constant feed to the system. When erected adjacent to reduction retorts, the molten metal from these retorts is taken directly to the melting pot without casting and it becomes a holding pot.

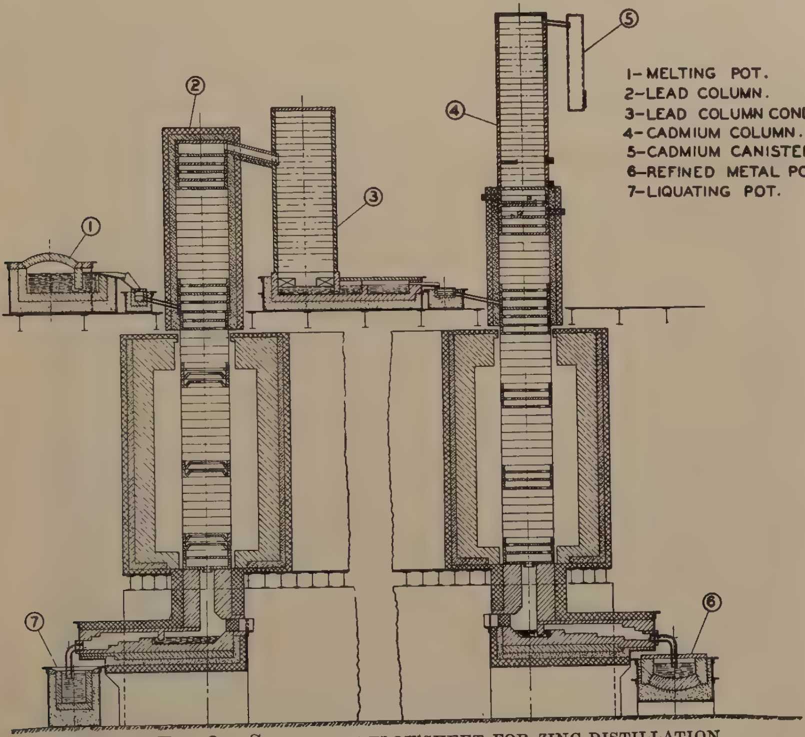


Fig. 2.—Schematic flowsheet for zinc distillation.

Automatic means for feeding crude metal at a uniform rate from the melting pot to the boiler is provided. The metal enters the boiler or "lead column" through a molten-metal seal, which prevents the escape of vapor. The vapor from the boiler ascends through a superimposed rectifying column for the elimination of lead and other high-boiling metals. The vapor, freed of these metals, passes to the condenser. The feed to the boiler is greater than the vapor output and the refluxed excess passes out through a molten-metal seal at the bottom of the boiler to a runoff pot. This may also serve as a liquating pot in which enough of the lead and iron, which usually constitute the bulk of the high-boiling impurities, may be separated to permit recirculation of the remaining zinc. This zinc is returned directly to the melting pot. This method of operation gives a maximum yield of the zinc in the feed metal as 99.99+ per cent pure zinc. Under certain market conditions, the runoff metal is sold to advantage as produced.

Molten metal from the condenser overflows through a liquid seal into the rectifying column for the removal of cadmium and other low-boiling impurities. The feed enters this column at a level appropriately chosen according to the composition of the feed metal, the product required and other factors.

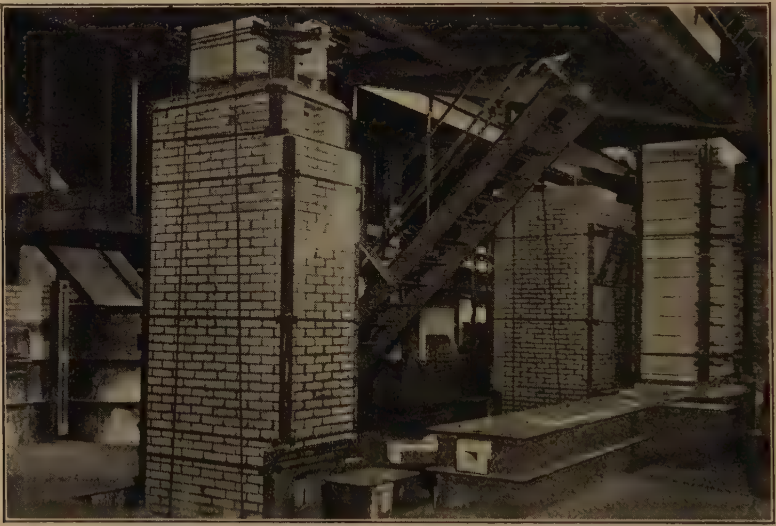


FIG. 3.—RECTIFYING COLUMNS AND CONDENSERS.

In this column, the condensing capacity at the top is adjusted to the boiling capacity in the bottom section, so that only a small proportion of the feed carrying the low-boiling impurities escapes at the top as vapor to be collected in a canister as dust or in a condenser as molten metal. The bulk of the feed, freed from low-boiling impurities and refluxed to the base of the column, escapes through a liquid metal seal to a refined-metal holding pot from which it is cast into slabs.

The photographs of a commercial plant show (Fig. 3) a 15-ton-per-day lead column in the right background, with its condenser on the extreme right and its sump in the foreground feeding a cadmium column on the left. The liquating pots for such units are shown in Fig. 4 and the refined-metal holding pots and the casting floor in Fig. 5.

Such a unit is adapted to continuous operation in such fashion as to reduce labor requirements to a minimum, the metal values can all be readily recovered, and losses are small since practically the entire operation is in a closed system.

Prime Western zinc in this country or G.O.B. metal in Europe constitutes the usual feed material, although any form of zinc metal that can be reduced to a liquid state can be treated successfully by the process, with a resultant product running as much above 99.99 per cent pure zinc as the requirements of the use may necessitate.

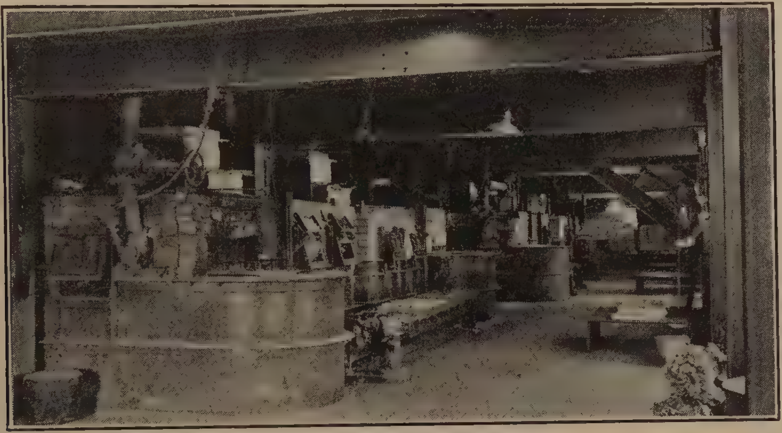


Fig. 4.—Liquating pots.

Temperature and oxidizing conditions present in the operation of the method are susceptible of close control, so that the formation of skimmings is held to a minimum. The direct production of high-purity zinc, when the runoff metal is recirculated, amounts to about 96 per cent of the zinc in the feed metal, and of the remaining 4 per cent, all except from 0.5 to 0.75 per cent is accounted for in the skimmings, dross and other by-products. The recovery of the zinc in the feed metal,

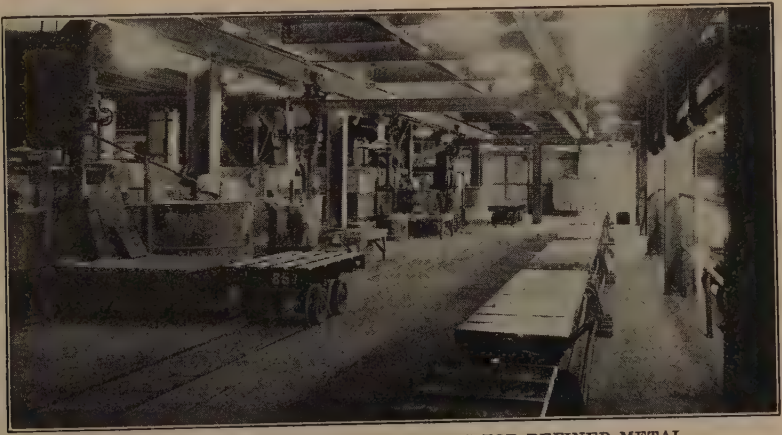


Fig. 5.—Casting floor, with pots for refined metal.

therefore, is in excess of 99 per cent. The cadmium comes off in the form of a cadmium-zinc metal or a cadmium dust, which is readily converted into metallic cadmium by any one of several known methods. Lead, copper, and any other metals present in the feed are recovered, and even the rarer metals, such as gallium and indium, if present, may be recovered.

Commercial installations are in operation in the United States, also in several other countries.

World Survey of Electrolytic Zinc

By Arthur Zentner,* Member A.I.M.E.

The electrolytic zinc plant of today is foreshadowed in the patents issued to Léon Létrange of Paris in 1881 and 1883[1]. He proposed roasting zinc blende to make the zinc soluble in water or sulphuric acid, thus obtaining a sulphate solution. His purification was apparently that used in the lithopone work of the day. For electrolyzing he proposed anodes of carbon or lead, for cathodes zinc, copper or brass. Numerous patents by other workers were taken out in the first 10 years, most of which dealt with sulphate solutions. It is easy to presume that the formation of chlorine gas in zinc chloride electrolysis caused early emphasis on sulphate work. Lack of success with this invited further work with chloride solutions. Efficient and cheaper oxidizing agents for use in the chloride processes were more generally available. Carbon anodes could be used instead of lead anodes, which were blamed for much of the early electrolyzing troubles and remained in disfavor for many years.

Carl Hoepfner received his first zinc patents in 1890[2]. He was the most persistent of those who worked with chloride solutions and met with the largest measure of success. He built three plants, only one of which remained in operation. This was built in 1896 at the plant of Brunner, Mond & Co., Winnington, England, now part of Imperial Chemical Industries Ltd. It leached with by-product calcium chloride from the company's Solvay alkali plant and returned to it the chlorine formed in electrolyzing. The zinc plant had a capacity of 5 long tons of zinc, said to have been doubled later, and remained in operation until 1924. No commercial plant using chloride solutions has operated since then.

E. A. Ashcroft experimented in the middle nineties with chloride, alkaline and sulphate solutions on materials from Broken Hill, Australia. He built a plant with a rated capacity of 10 long tons of zinc per day, at Cockle Creek, New South Wales, in 1898. This figure was never approached nor was cyclical operation achieved. The work in the plant appears to have been largely with sulphate solutions. The plant suffered from a multitude of troubles: poor roasting, gelatinous silica, liberal use of live steam in solutions to combat the gelatinous silica with considerable

---

Manuscript received at the office of the Institute Nov. 2, 1936.

* Consulting Engineer, New York, N. Y. and San Francisco, Calif.

[1] German Patent D.R. 21775 (July 8, 1881), British Patent 3211 (July 22, 1881), U. S. Patent 286208 (Oct. 9, 1883).

[2] German Patent D.R. 65478 and 68748.

oil getting into the circuit with the steam, inability to keep the wash water within bounds, poor purification practice, the use of antimonial lead for anodes, were some of them.

S. O. Cowper-Coles became interested in treating the Broken Hill complex ores and middlings. He built an electrolytic zinc pilot plant in England in 1895, and apparently worked on the problem until 1899, using sulphate solutions. Aluminum cathodes were used for the first time in this plant, a notable contribution.

The proposal to electrolyze fused zinc chloride dates back to Nahnsen's early work and was pursued by workers in several countries before the turn of the century. After his Cockle Creek work, Ashcroft, with James Swinburne, developed one of these, and in more recent years the Ashcroft-Lacell process.

The Siemens-Halske company spent a greal deal of time and effort on electrolytic zinc, much of it in the early years in trying to leach sulphide ores without roasting, made a number of contributions to the art and was still pursuing the subject of commercial electrolytic zinc under the direction of Dr. Victor Englehard when the Anaconda Copper Mining Co. and the Consolidated Mining and Smelting Co. went into commercial production.

Like Siemens-Halske, S. Laszczynski was led, at the close of the century, to investigate electrolytic zinc by doing similar work on copper. A little later W. Stöger worked the Laszczynski process in a pilot plant and recorded some advances; among them, electrolyzing in sulphuric acid up to 9 per cent. This seems to be the first account of pilot-plant work with sulphate solutions that was not harassed continually by spongy zinc deposits or uncontrollable resolution of zinc deposits. The significance of the acid bath does not appear to have been stressed in accounts of the work. The idea that the cell solution in electrolyzing zinc must be kept neutral, or nearly so, persisted in several quarters until after 1910.

Attempts in several countries to develop a commercial process and plant continued without much success until the war. The rapid rise in prices and premiums offered for pure zinc intensified the search. The staff of the Anaconda Copper Mining Co., under the leadership of Frederick Laist, and that of the Consolidated Mining and Smelting Co., Ltd., under the leadership of Selwyn G. Blaylock, developed processes and plants that continued and increased production after the war. The spread of electrolytic zinc production over the world began and has continued to the present time. There are now completed or under construction 24 electrolytic zinc plants (Table 2 and Fig. 4), all using sulphate solutions.

This is a very brief statement, with many omissions, of the rise of electrolytic zinc from its inception to the present. A more extended account could include the interesting story of other early work and workers.

In Table 1, the year 1913 shows the status of production of zinc metal before the war with no electrolytic zinc plants operating in the United States and most of the small world production coming from the Brunner, Mond plant in England. The years 1914 to 1918 show the rapid emergence of electrolytic zinc into commercial production, more rapid in the United States than elsewhere. In 1921 foreign production rose above United States and has that of the remained above; in fact, outstripping it

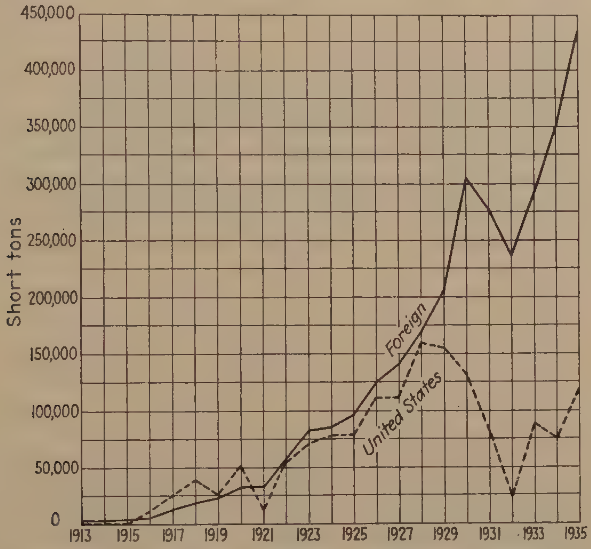


FIG. 1.—WORLD PRODUCTION OF ELECTROLYTIC ZINC.

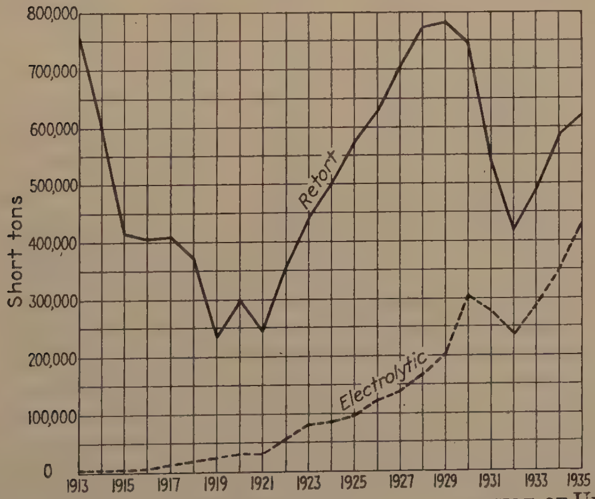


FIG. 2.—ELECTROLYTIC VS. RETORT PRODUCTION OF ZINC OUTSIDE OF UNITED STATES.

since 1928. The foreign production in 1935 was 79 per cent of the world production. The capacity of plants in the United States is around 231,000 short tons and that of plants outside of the United States about 560,000 short tons, including those of the U.S.S.R., indicating a foreign capacity of 71 per cent of the world electrolytic zinc plant capacity. Fig. 1 shows the great increase in the production of electrolytic zinc outside the United States since 1928, broken only by the relatively small decrease in 1931 and 1932. This may also be seen in Fig. 2, which compares it to foreign retort-zinc production. In 1929, foreign electrolytic production was only 26 per cent of foreign retort production; in 1935, it was 70 per cent—striking evidence that electrolytic zinc in foreign countries has come out of the depression years in a far stronger position than it entered them.

TABLE 1.—*World Zinc Production*[a]

SHORT TONS

Year	Total			Electrolytic			Retort	
	World	U. S.	Foreign	World	U. S.	Foreign	U. S.	Foreign
1913	1,113,872	352,952	760,920	3,500		3,500	352,956	757,420
1914	968,207	370,200	598,007	3,500		3,500	370,200	594,507
1915	924,977	507,004	417,973	3,752	252	3,500	506,752	414,225
1916	1,089,980	679,833	410,147	17,600	11,116	6,484	668,717	403,663
1917	1,105,826	682,225	423,601	38,700	25,209	13,491	657,016	410,110
1918	914,474	525,349	389,125	58,490	38,916	19,574	486,433	369,551
1919	728,927	471,684	257,243	50,711	27,056	23,655	444,628	233,588
1920	811,537	479,669	331,868	84,968	51,626	33,342	428,043	298,526
1921	493,439	215,614	277,825	43,936	11,559	32,377	204,055	245,448
1922	792,777	373,678	419,099	113,853	55,369	50,484	318,309	360,615
1923	1,059,821	531,202	528,619	153,804	71,088	82,716	460,114	445,903
1924	1,125,188	535,846	589,342	163,405	77,493	85,912	458,353	503,430
1925	1,265,714	590,928	674,786	175,601	79,004	96,597	511,924	578,189
1926	1,373,212	638,533	734,679	236,143	111,596	124,547	526,937	610,132
1927	1,464,091	613,548	850,543	253,262	112,629	140,633	500,919	709,910
1928	1,566,919	619,595	947,324	329,686	160,160	169,526	459,435	777,798
1929	1,623,451	631,601	991,850	362,056	156,235	205,821	475,366	786,029
1930	1,556,857	504,463	1,052,394	437,221	131,188	306,033	373,275	746,361
1931	1,111,450	300,738	810,712	362,148	82,210	279,938	218,528	530,774
1932	870,758	213,531	657,227	260,857	23,208	237,649	190,323	419,578
1933	1,106,864	324,705	782,159	377,967	88,315	289,652	236,390	492,507
1934	1,305,052	366,933	938,119	425,418	76,657	348,761	290,276	589,358
1935	1,487,383	431,499	1,055,884	552,270	118,476	433,794	313,023	622,090

[a] The figures in this table are variously from the American Bureau of Metal Statistics, American Zinc Institute, U. S. Geological Survey and U. S. Bureau of Mines, or have been supplied by the author.

In the United States the 1929 production of electrolytic was 33 per cent of retort production; in 1935, it was 38 per cent. Actually the picture is better than shown in Fig. 3, as the stock on hand of electrolytic zinc decreased since 1929, while that of retort zinc increased.

The status of electrolytic zinc up to 1929 is given in an article by the writer in the November, 1929, issue of MINING AND METALLURGY (pp. 526–531), so that mainly the developments since 1929 will be stressed here.

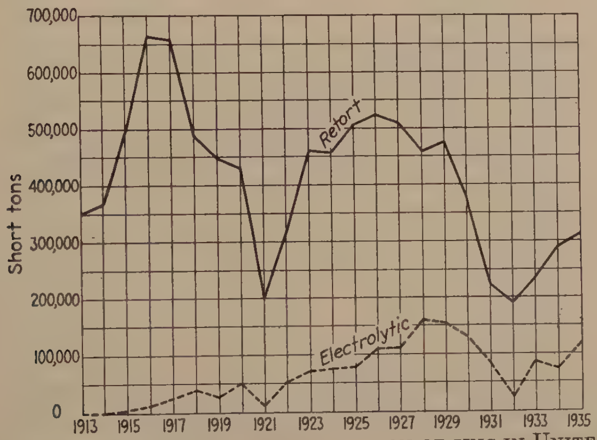


FIG. 3.—ELECTROLYTIC VS. RETORT PRODUCTION OF ZINC IN UNITED STATES.

Table 2 shows the electrolytic zinc plants now operating or in process of construction, their capacities and productions for 1929 and 1935.

CANADA

The Consolidated Mining and Smelting Co., Ltd., built a 35-ton (cathode zinc per day) electrolytic zinc plant at Trail, B. C., and started commercial production early in 1916. Several additions have been made, until now it is the largest single plant in the world, with a capacity of 400 tons per day. The main source of raw material is concentrate derived from the Sullivan mine of the company at Kimberley, B. C. A description of the plant is given in this volume (pp. 540 and 721), with its special features, such as two circuits treating calcine and fume from lead blast-furnace slag, the plant producing this fume, and the flash roast. All Canadian power is hydroelectric, of course. The 1929 production was 86,049 short tons of ingot zinc; in 1935, it was 119,051 tons.

The Hudson Bay Mining and Smelting Co., Ltd., built a 70-ton zinc plant at Flin Flon, Manitoba, which began producing in 1930. The capacity was increased by 10 per cent in 1933, and by adding a fourth unit to the cell room in 1935, so that it might now be called a 100-ton plant. The zinc-plant feed, derived from the company's Flin Flon mine, contains more copper than that treated by any other plant except that of the Cheliabinsk plant in the U.S.S.R. Also, it contains practically no lead,

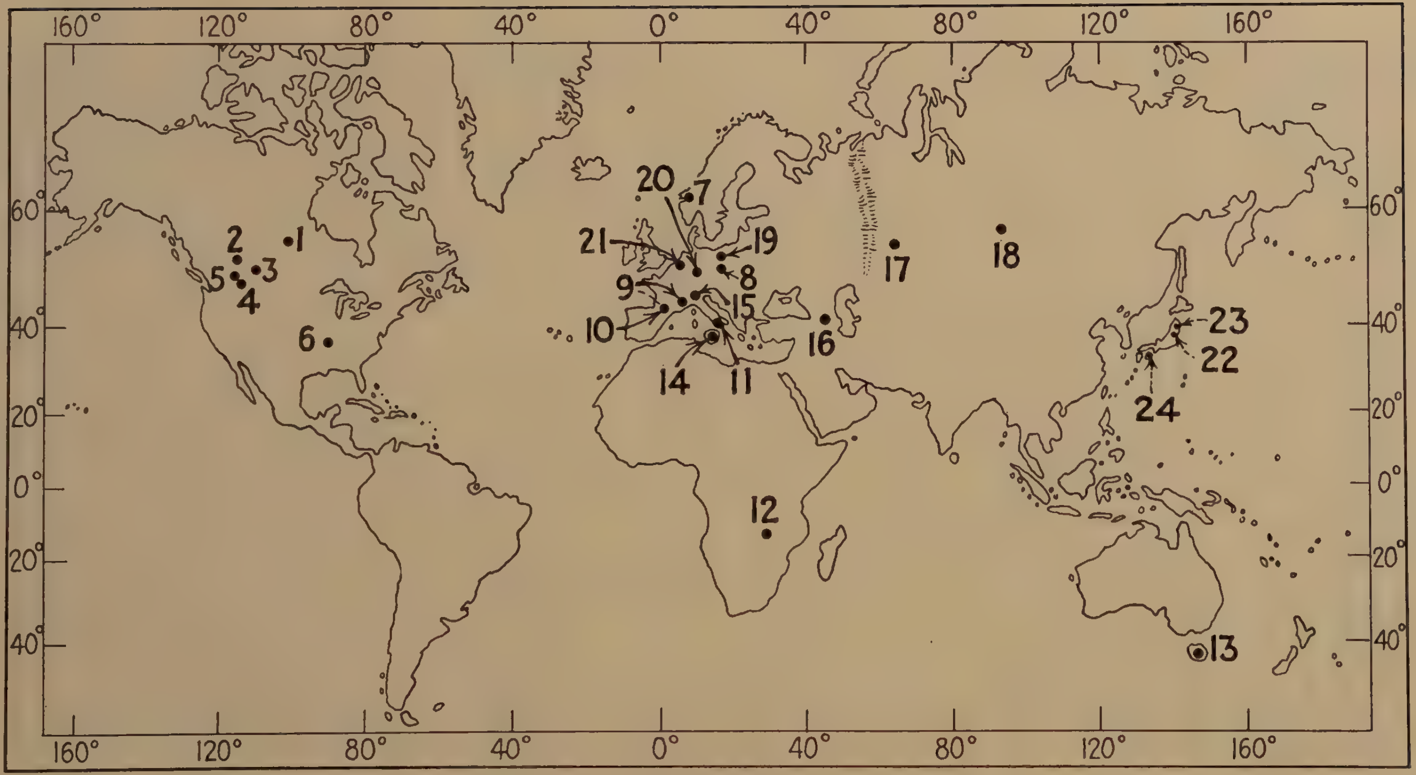


FIG. 4.—LOCATIONS OF ELECTROLYTIC ZINC PLANTS.

1. Flin Flon (Hudson Bay).
2. Consolidated.
3. Anaconda Copper Mining Co. (Great Falls).
4. A.C.M. (Anaconda).
5. Sullivan.
6. Evans-Wallower.
7. Norske Zinkkompani.
8. Giesche Spólka Akcyjna (Polish).
9. San Dalmazzo (Liguri).
10. Vieille Montagne (France).
11. Pertusola.
12. Rhodesia Broken Hill.
13. Electrolytic Zinc Co. of Australasia.
14. Monteponi.
15. Montecatini-Montevecchio.
16. Ordzhonikidze.
17. Cheliabinsk.
18. Kemerovo.
19. Slaskie Kopaline i Cynkownie.
20. von Giesche's Erben (German).
21. Vieille Montagne (Belgium).
22. Nippon Soda.
23. Hosokura.
24. Naoshima.

and is higher than normal in iron. Some of the unusual features are the roasters designed for a split draft, precipitation of the bulk of the dissolved copper on slab zinc and the use of electrolytic zinc castings for a variety of plant purposes. The plant has been fortunate in not having to run on

TABLE 2.—*Electrolytic Zinc Plants*

	Capacity, Short Tons Cathode Zinc per Day	Production, Short Tons Ingot Zinc per Year	
		1929	1935
Canada:			
Consolidated Mining & Smelting Co. Ltd	400	86,049	119,051
Hudson Bay Mining & Smelting Co. Ltd	100		30,052
Norway:			
Det Norske Zinkkompani A. S	150	6,474	49,604
U.S.S.R.:			
Ordzhonikidze plant	60		17,600
Cheliabinsk plant	60		
Kemerovo plant	150		
Poland:			
Giesche Spolka Akcyjna	66	14,518	22,133
Slaskie Kopaline i Cynkownie	22		
Germany:			
Georg von Giesche's Erben	120	522[a]	42,230
France:			
Vieille Montagne	110	17,200	24,438
Belgium:			
Vieille Montagne	22		2,066
Italy:			
Cia Impresa Elettriche Liguri	10	10,551	19,713
Società di Monteponi	20		
Società Mineraria e Metallurgica di Pertusola	36		
Società Montecatini-Montevecchio	30		
Japan:			
Nippon Soda Co	20	941	5,000
Mitsubishi Mining Co., Hosokura plant	9		2,542
Mitsubishi Mining Co., Naoshima plant	20		1,387
Rhodesia:			
Rhodesia Broken Hill Development Co., Ltd	70	13,575	23,102
Australia:			
Electrolytic Zinc Corporation. Australasia, Ltd	225	56,001	74,856
U. S. A.:			
Anaconda Copper Mining Co., Great Falls	340	82,020	106,028
Anaconda Copper Mining Co., Anaconda	170	55,990	
Sullivan Mining Co	65	16,582	12,448
Evans-Wallower Zinc Co	50	1,634	

[a] Pilot-plant production.

a closed circuit. A portion of the neutral solution is used in the mill for flotation, and a portion of the cell acid (stripped of zinc) is discarded to keep the SO_4 content from building up too high. The production in 1931, the first full year, was 17,528 tons; in 1935, it was 30,052 tons.

NORWAY

The Norske Zinkkompani's zinc plant is at Eitrheim, not very far from Bergen, Norway. This plant was built under the guidance of the Anaconda company and came into production in 1929. Most of the concentrate comes from the Reocin (Spain) mines of the Asturienne company and is roasted in Belgium for manufacture of sulphuric acid before being shipped to Norway. The concentrate carries sufficient magnesium to require discard of solution in order to keep the magnesium content within limits. The plant was built for a production of 110 tons, from three cell-room units, and has been since increased by one-third. The production in 1930, the first full year, was 41,054 tons; in 1935, it was 49,604 tons.

UNION OF SOVIET SOCIALIST REPUBLICS

The U.S.S.R. plans for production of electrolytic zinc have undergone several changes. A one-ton (zinc per day) pilot plant was built at the Ridder mine and operated for some time. Eventually the first commercial plant was built at Ordzhonikidze, in the Caucasus, for a rated capacity of 10,000 metric tons of slab zinc per year, and has been doubled in capacity. A main source of feed is the Mizursky mine, near at hand; a lead-zinc ore from which a zinc concentrate is obtained. Among special features are mercury-arc rectifiers for converting electric power into direct current. This plant came into production in 1934 with 5980 short tons. In 1935 production for this plant and for the Cheliabinsk plant was about 17,600 short tons.

The second U.S.S.R. plant to be built was the one at Cheliabinsk, in the Urals, with a rated capacity of 20,000 metric tons of slab zinc per year. The zincky ores of the Urals run to copper, rather than lead, with the zinc. The copper is difficult to separate satisfactorily. The result for the zinc plant is a concentrate that is higher in copper than perhaps any other being treated in a similar manner. The plant came into production in 1935.

A third plant has been planned, to be built at Kemerovo, in the Kuzbass region in Siberia, and to have a capacity of 50,000 metric tons of slab zinc per year. The feed is to be concentrate mainly from lead-zinc ores of surrounding districts including the well-known Ridder mine.

POLAND

Upper Silesia, now in Poland, has been the scene of attempts to develop a commercial electrolytic zinc plant for many years. It remained for the

Anaconda company, through the Giesche Spólka Akcyjna, to build the first one at Szopienice, near Kattowice, in 1928. This was based upon its work in the United States of America. It was built for a capacity of 66 tons. The feed is a high-grade concentrate from the company's mine near by. Originally the plant operated on a Waelz fume obtained from oxidized ore and tailings, and the concentrate went to the company's retort zinc plant. It was found beneficial to both plants to switch the two feeds. The electrolytic zinc plant is said to be able to compete with the retort plant on even terms as to costs and actually to assist in reducing the cost of operation of the retort zinc plant. The former receives its electricity from a coal-burning generating plant, which uses the reject from coal screenings. The retort plant receives the screened coal at a lower cost because the electrolytic plant can use the reject coal. The production in 1929, the first full year, was 14,518 tons; in 1935, it was 22,133 tons.

The Slaskie Kopalnie i Cynkownie, Spólka Akcyjna, has a plant at Kamién, Poland, with a rated capacity of 22 tons. A production of 2705 tons is given for 1930. Since then it appears to have been idle most of the time, if not all.

GERMANY

The Georg von Giesche's Erben, mining the part of the von Giesche property that was left on the German side of the Polish-German boundary, built a 120-ton plant to treat the concentrate at Magdeburg, in conjunction with the German Government. The plant is described in another part of this volume (p. 465). It includes a number of innovations. The power is coal-generated by a plant across the canal from the zinc plant. The production in 1935, the first full year, was 42,230 tons.

FRANCE

Vieille Montagne began planning a zinc plant before the war ended and finally build a small one at Viviez, in southern France, which began producing in 1923. The capacity was increased and the output in 1929 reached 17,200 tons. The capacity has been further increased, so that it is now a 110-ton plant. The output in 1935 was 24,438 tons.

BELGIUM

Vieille Montagne has built another plant at Baelen, Belgium, which came into production in 1935. It is a 22-ton plant, which treats the zinc fume from the company's lead-furnace slag-fuming plant. The production for 1935 was 2066 tons.

ITALY

Italy has four small plants, including the one under construction by Montecatini-Montevecchio at Porto Marghera, near Venice. It is to have a capacity of 10,000 metric tons per year.

Italian work started in 1916 and drew upon the research work of Laszczynski, Stöger and Siemens-Halske. The first commercial production, if it could be called that, was in 1921 from the Cia. Impresa Elettriche Liguri plant at San Dalmazzo di Tenda, near Genoa. It is a 10-ton plant and has lain idle for more than five years. The feed was roasted sulphide material, some of which came from the Miniera di Vallauria near by and ores of Lombardy. Hydroelectric power from a near-by source was used.

The Società di Monteponi built the second plant at Monteponi, Sardinia, to treat the low-grade, iron-bearing calamines of that company's Campo Pisano mines. It is a 20-ton plant and came into production in 1926. A pyrite-roasting acid plant supplies the acid required.

The third plant was built by the Società Mineraria e Metallurgica di Pertusola near Crotone. It is a 36-ton plant built under the guidance of the Anaconda company, and came into production in 1928. It also treats material from Sardinia but in large part the feed is a blende from the Miniera Ingurtosa, which is roasted at Crotone for manufacture of sulphuric acid.

The total production in Italy in 1929 was 10,551 tons; in 1935 it was 19,713 tons.

JAPAN

Japan started work on electrolytic zinc as early as 1917 with a mill built by the Nippon Soda Co. at Fukushima-Ken. This was what might be called a pilot plant, with a capacity of 2 tons per day. Apparently it was none too successful, and a second one was built a few years later. Production seems to have remained at 1000 tons or under until 1931. The capacity is now given as 20 tons per day and the output was estimated in 1935 as 5000 tons.

A second plant, built by the Mitsubishi Mining Co. near the Hosokura mine, Miyagi Pref., had an estimated production of 2000 tons in 1932 and 2542 tons in 1935. A third plant, also built by the Mitsubishi Mining Co., is near Naoshima, Kagawa Pref. It came into production in 1935 with 1387 tons and is rated as a 20-ton plant.

RHODESIA

Rhodesia Broken Hill Development Co. started work on a plant to treat calamine from its deposit in Northern Rhodesia. It is south of the large copper deposits. The plant came into production in 1928, rated as a 35-ton plant. It has been enlarged and is now rated at over 70 tons. The ore contains vanadium, which is separated and sold as a by-product. The zinc is present as a silicate, which means a large amount of soluble silica, as at the Monteponi (Italian) plant. It averages only 25 per cent zinc. Slag from previous lead-smelting operation is used as the source of soluble iron in the leach, giving still more soluble silica. Satisfactory handling of this silica and recovery of the vanadium content are creditable achievements.

Production in 1929 was 13,575 tons; in 1935 it was 23,102 tons. The plant shut down in June 1931 but reopened at the beginning of 1932.

AUSTRALIA

Electrolytic Zinc of Australasia Ltd. came into production in 1918 after benefiting from work in the United States. Increase in capacity of the plant was begun in 1929 but held in abeyance until 1935. It is now rated as a 225-ton plant. With the adoption of the alkaline circuit in flotation mills of the Broken Hill district a few years ago, the grade of the zinc concentrate to this plant has steadily risen in zinc to over 50 per cent and fallen off in lead and silica content. One wonders if the change in the concentrate will cause changes in the zinc plant. A description of the plant is given elsewhere in this book (p. 482).

Nearly all the Broken Hill concentrate is roasted on the Australian mainland for sulphuric acid production. The calcine is then shipped to the zinc plant at Risdon, Tasmania. Raw-material requirements for the increase in plant are being met in large part by concentrate from the Rosebery and Hercules ores of the company near Zeehan, Tasmania.

The production in 1929 was 56,001 tons; in 1935, it was 74,856 tons.

UNITED STATES OF AMERICA

Commercial production of electrolytic zinc in the United States began in the 10-ton plant of the Anaconda company at Anaconda, Mont., late in 1915. Shortly this was enlarged to a 25-ton plant. Meanwhile the 100-ton plant was being built at Great Falls, Mont. The latter was enlarged in several steps to reach a capacity of 340 tons per day 10 years later. The 25-ton plant at Anaconda was dismantled in 1916 and some of the equipment used in the first enlargement of the Great Falls plant. In 1927 a new 170-ton plant was built at Anaconda. The feed for these plants is concentrate from company and outside sources, mainly Montana, Utah and Idaho. In addition, the Great Falls plant continues to treat fume from lead blast-furnace slag from the plant at East Helena. Production of these two plants amounted to 138,010 tons in 1929, and of the Great Falls plant to 106,028 tons in 1935. The Anaconda plant was started up at half capacity in June 1936, after a three-year shutdown. Zinc was being made in half a month after the order to start was received.

The Sullivan Mining Co., at Kellogg, Idaho, built a 65-ton plant to operate on the Tainton electrolytic zinc process and started up late in 1928. The feed is zinc concentrate from the company's Star mine and a number of outside sources. A description of the plant may be found elsewhere in this volume (p. 527). Production in 1929 was 16,582 tons; in

1935, it was 12,448 tons. Production this year, 1936, has been practically at full capacity.

The Evans-Wallower Zinc Co. also built a plant for using the Tainton process; a 50-ton plant at East St. Louis, Ill., which started up late in 1929. A number of concentrates and other materials were used as feed. Production in 1930 was 9516 tons; in 1931, it was 10,654. Since then the plant has not operated.

ELECTROGALVANIZING

A notable development since 1929 has been the commercial production of a finished article from electrolytic zinc plant purified solution—namely, electrogalvanized wire. Production of solution and electrolysis is essentially by the Tainton process, using a much higher current density than in the Tainton electrolytic-zinc process. Bethlehem Steel is now operating a plant rated at 250 tons of wire per day, at Johnstown, Pa.

PURITY OF PRODUCT

Beside the large increase in the production of electrolytic zinc since 1929, the development of the industry has been characterized by continued increase in the purity of the metal produced. Electrolytic zinc of 99.99+ per cent grade is now produced in low, medium, and high current-density plants.

The Magdeburg Zinc Works of the Georg von Giesche's Erben Mining Company

By Hermann Bach,* Walther Hänig,† Willi Gehrhardt,‡ Ernst Theurich§ and Walter Langner||

With the construction of the Magdeburg zinc works, the Georg von Giesche's Erben Mining Co. of Breslau has to a certain extent completed the program of reconstruction which it set as its goal after the boundaries of Upper Silesia were drawn by the Treaty of Versailles. During its history, covering more than two centuries, zinc and lead mining has been its chief activity. Through the new boundaries established, it lost to Poland all its mines and smelters, including five distillation smelters. Of its extensive properties, there remained only an apparently unimportant and unexplored portion of the old Bleischarley ore field which, however, happily made possible the resumption of its old business. In 1925 the Deutsch-Bleischarley shaft—only a few kilometers from the old Bleischarley shaft—was sunk and developed, and in May 1926 production of lead and zinc ore was resumed. As facilities for smelting were lacking, the ore was at first delivered to the neighboring smelters, which had now become Polish. Realization of the plan to build its own zinc works had to be postponed at first for lack of capital. In the meantime, however, plans for the new works were worked out in all details.

After extensive experimentation in a semicommercial pilot plant it was decided, at the end of 1928 and the beginning of 1929, to use the electrolytic process and, for economic reasons, to place the works at Magdeburg. With zinc at the approximate price level that had ruled since the Deutsch-Bleischarley mine had begun working, it was hoped that the plan could be completed in 1930 with the company's own resources. However, falling metal prices, already noticeable in 1929, made this impossible, and further postponement for a time became necessary. Finally, at the end of July 1933, the funds for building the works became available, in the form of a loan granted under the first employment

---

Manuscript received at the office of the Institute Aug. 10, 1936.

[*] General Superintendent, Magdeburg Plant, Georg von Giesche's Erben, Germany.

[†] Assistant Superintendent.

[‡] Superintendent Roasting and Acid Manufacture.

[§] Superintendent Leaching and Electrolyzing.

[||] Superintendent Residue Treatment and Cadmium Plants.

program of the National Socialist Government. Only a few days later, on Aug. 1, 1933, construction of the Magdeburg zinc works was begun, and after a building period of one year, including clearing of the site, it was ready for operation.

The zinc works was erected in the new industrial region of Magdeburg, about 10 km. north of the city. The plant site lies in the area created by excavation and dredging for the Magdeburg industrial harbor. This harbor lies on the canal connecting the Elbe and the Mittelland canal, which is still under construction. The site was formerly in the flood area of the Elbe and was filled in with earth from the dredging operations for the harbor.

Careful investigation of the ground, chiefly by borings, showed the use of pile foundations to be necessary. Altogether, about 22,000 running meters of Mast system (steel-shell) piles were driven, part of which had to be driven 14 m. deep. The electrolyzing plant was not erected on piles, because deep excavations were required for the cellar under the cell room. As this cellar lies below the high-water level of the Elbe, it was built of reinforced concrete as a waterproof chamber.

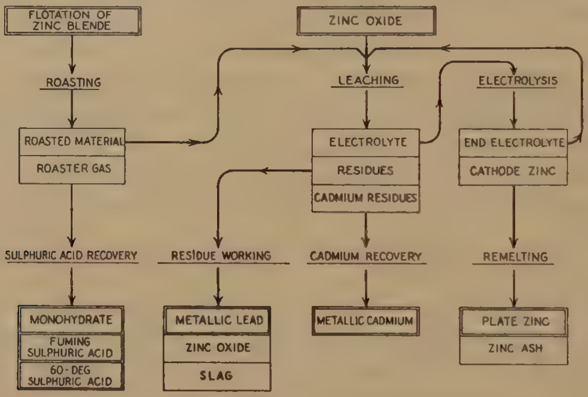


FIG. 1.—FLOWSHEET OF ZINC WORKS.

The works property has an area of 500,000 sq. m. and has water and rail connections. The buildings are arranged according to the flowsheet (Fig. 1), along a main road connected to the public highway system.

In addition to the plants for the actual zinc extraction, the roasting plant with its associated sulphuric acid works, the leaching plant, electrolytic plant and plant for melting the cathodes, there is a cadmium plant for working up the cadmium residues from the zinc solutions, and a residue plant for treating the zinc and lead residues from the leaching plant. A year ago a zinc-alloy plant was added, in which zinc alloys containing aluminum, copper and magnesium with a base of electrolytic zinc are made for die-casting. Auxiliary plants are the central workshop, the water works and purification plant, the warehouse for spare parts and material, the sample mill, the chemical and metallurgical laboratories and, finally, the change house with the arrangements for social welfare.

The necessary electrical power and the heating and process steam are purchased from a steam-power plant about 200 m. from the works. Three-phase 10,000-volt current is received and transformed at the works into three-phase 500-volt current, or rectified into direct current for electrolysis.

The works were planned for a yearly production of 40,000 tons of electrolytic zinc and 65,000 tons of 66° sulphuric acid and were brought to full capacity after a breaking-in period of about three months. Up to the present, only flotation blende from the Deutsch-Bleischarley mine has been worked, in addition to the zinc oxide made in the residue plant and the dechloridized zinc dross from the melting plant. The blende contains 8 to 10 per cent moisture when delivered and has approximately the following composition, calculated to dryness: Zn, 60 to 62 per cent; S, 32 to 33; Pb, 1; Cd, 0.2 to 0.25; Fe, 3; Cu, 0.055; Ni, 0.004; Co, 0.002; SiO_2, 0.22; CaO, 0.17; MgO, 0.15; Al_2O_3, 0.04; Mn, 0.015; As, 0.12, Cl, 0.12.

The flotation blende, with a fineness of 96 per cent below 0.25 mm. and 65 per cent below 0.1 mm., is lumpy and gritty when unloaded. Even after partial preliminary drying on the drying hearth of the roasting furnaces, these lumps do not disintegrate, but pass through the furnace only superficially roasted and lower the extraction. With insufficient preparation of the raw blende, the proportion of badly roasted lumps may amount to 25 per cent, but with proper preparation it is below 10 per cent, and at the same time a better calcine and an improvement in the fuel consumption is obtained. The physical condition of the blende is most favorable when it contains about 4 per cent of moisture. Such a blende is not lumpy but soft and loose. Drying below 4 per cent is not desirable, as absolutely dry blende forms too dense a layer on the upper hearth of the roasting furnaces, flows too easily across the hearth and will form more dust. For this reason drying of blende was introduced ahead of the roasting.

DRYING PLANT

The blende received by rail or water is unloaded from the cars or barges, or taken from the stockpile by a grab crane having a capacity of 2 cu. m., and delivered to a hopper discharged by a pulsating push-feeder to a belt conveyor with a capacity of 100 to 120 tons per hour, which discharges into a 400-ton stock bin. The raw, wet blende is then delivered by a push-feeder to a steam-heated hearth drier 5 m. in external diameter, with six hearths. The blende is carried accross the individual hearths by six rabble arms. The drier has a capacity of about 12.5 tons per hour and reduces the moisture to 2 to 4 per cent H_2O with a steam consumption of 0.8 to 1.2 tons per hour, depending on the degree of drying. The dust in the escaping vapor is removed in a combination wet and dry separator. The escaping gases contain less than 0.5 grams per cubic meter of dust. The dried material is reduced to uniform size in a centrifugal mill and then carried by a belt conveyor and an elevator to an intermediate storage bin, or distributed directly, after weighing on an automatic scale, to the feeding hoppers above the roasting furnaces.

Roasting Plant

For roasting the flotation blende, four nine-hearth Humboldt mechanical roasting furnaces have been provided (Fig. 2). During the roasting the blende progresses through the furnace in the usual way over the inner and outer drop-hole hearths. The roasted blende after discharging passes a screen with meshes about 20 mm. wide. The oversize lumps are collected in a special car and ground in an edge runner. The screened fines discharge down a water-cooled chute into a push conveyor under the floor in front of the furnaces and are cooled there to about 80° C., which is necessary to protect the screening equipment.

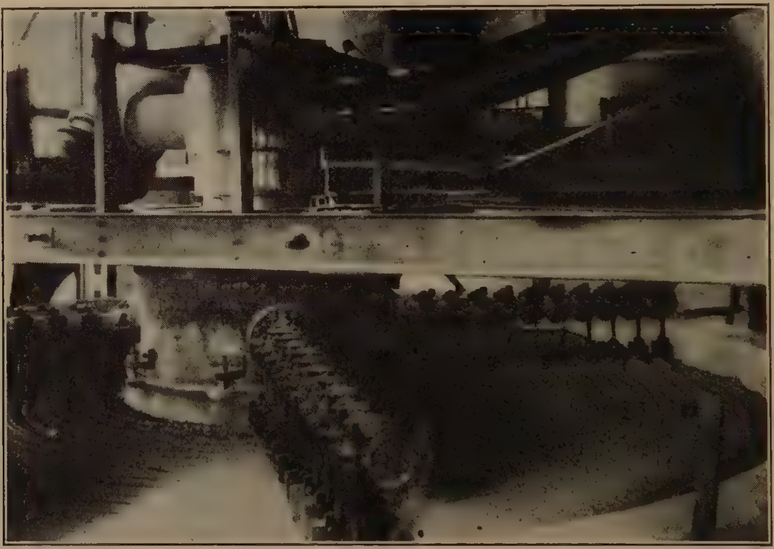


Fig. 2.—Head of roasting furnace.

For screening the calcine, four vibrating screens, with a screen area of 1000 by 2000 mm. each, are placed above the storage bin, two being in use and two in reserve. The undersize falls into a double bin having a capacity of about 400 tons. From this the calcine is fed to a bucket conveyor by an inclosed rotary feeder, and after being weighed automatically, is conveyed by a belt conveyor to the leaching plant. Oversized material goes into a small bin, from which an inclosed rotary feeder carries it to a screenless ball mill having a capacity of about 3.5 tons per hour. Depending upon the degree of desulphurization, the oversized material is either mixed with finished calcine or sent back to the furnace charge.

The dust deposited in the gas collectors near the gas outlets, in the cyclones and the balloon flue and in the Cottrell treater is transported by a pneumatic conveyor and is mixed with the calcine if suitable. If the dust contains more than 0.5 per cent of sulphur as sulphide or more sulphur as sulphate than is permissible, it is returned to the roasting plant.

The roasting furnaces were designed for a daily feed of 60 tons of raw blende each. With normal charging, about 50 to 55 tons, there is a sufficient reserve capacity to permit of necessary repairs.

The furnaces have an external diameter of 7600 mm. and an internal one of 6500 mm. The internal diameter of the center shaft is 1600 mm. and the external 2000 mm. The firebrick lining is 550 mm. thick and insulated at all nonsupporting points. The furnace has a drying hearth and nine roasting hearths. The hearths are built flat to give as little dead hearth layer as possible, thus avoiding the formation of thick crusts. Maximum use is made of the principle that more roasting is done during the fall of the ore from one hearth to the next. The hearths that discharge at the center are provided with a ring discharge 3000 mm. in diameter, the material falling in a thin stream onto the next hearth. The hearths that discharge to the periphery each have 10 large drop-holes. On hearths 5 to 9, the cross sections of the drop-holes and rings are restricted. These points, together with the masonry construction, and the method of introducing the air, account for the high capacity of the furnaces.

The drier hearth has four rabble arms to insure even feeding to the first roasting hearth. The roasting hearths have two rabble arms each. The individual rabbles have a blade angle of 60° on the upper hearths (1, 2, 3 and 4) and of 70° on the lower (5, 6, 7, 8 and 9), in order to pile up the material especially on hearths 7 to 9 and slow down the passage of the ore. By this means, the evolved heat is better utilized and the last traces of sulphur more positively removed. The furnace is direct driven through two sets of gears. For greater flexibility and for better control of the roasting, the time for one revolution may be varied at will from 1 to 2 min., giving a roasting time of 5 to 10 hr., respectively.

One of the most important features, in addition to the internal construction of the furnaces and the various structural details, is the method of introducing the roasting air. Each furnace has a cold-air fan, which delivers 175 cu. m. per min. of air at a pressure of 300 mm. of water. The air for cooling the rabble arms is utilized as preheated roasting air and is distributed to the various hearths according to a scheme established by experimentation.

The bottom hearth (No. 9) is heated in addition by industrial gas. Expressed as fuel oil with a calorific value of 10,000 cal., the gas consumption is 1 per cent. This is necessary to obtain a uniform product containing about 0.3 per cent of sulphur as sulphide and less than 1 per cent as sulphate, with the iron thoroughly oxidized and a complete volatilization of the arsenic and chlorine.

As mentioned, the furnaces were designed for a daily capacity of 60 metric tons of raw blende each. Actually, 64 tons per day are roasted in each furnace. With a feed of 31 per cent S, about 20,000 kg. S is roasted off on 248 sq. m. of effective hearth area in 24 hr. Differently expressed, the roasting capacity is 80 kg. of sulphur or 258 kg. of dry blende per square meter per day. About 13 per cent of the feed is recovered as flue dust. Half of the dust is well roasted and may be added to the calcine; 20 per cent is recovered in the Cottrell treater and sent to the residue plant, which is described later. The remainder is returned to the furnaces.

The roaster gases drawn off from the four upper hearths on two sides of the furnaces have a concentration of approximately 6 per cent SO_2 by volume. Part of the accompanying dust is recovered in the cyclone situated close behind the roasting furnaces, and in the balloon flue, which also serves to equalize the furnace draft. The dust collected there returns to the roasting plant. The remaining dust, 6 to 8 grams per cubic meter, is collected in a Cottrell treater, where the temperature averages about 450° C.

Sulphuric Acid Plant

The dust precipitator ahead of the contact acid plant consists of three Siemens-Lurgi-Cottrell chamber systems connected in parallel. The operating voltage is 52,000 volts at 80 to 100 milliamperes. The clearance is 99 per cent, so that the purified gas contains less than 0.5 gram of dust per cubic meter. The average velocity of the gas through the chambers is 0.5 meter per second.

After the dust precipitation, the gases enter the washing and cooling equipment, which consists of three parallel tower systems, each system containing two lead towers in tandem. The rising gas is sprayed in the first tower with 50° Bé. acid, lowering the temperature to about 100° C. This tower is lined with acidproof brick but contains no packing. The second tower is lined at the bottom quarter only. About this point it is packed with acidproof rings. The washing is done with 5° Bé. acid and effects a cooling to 40° C.

The scrubbed and cooled gas then enters the final or de-arsenifying treater, where it is freed from the last traces of lead, arsenic, SO_3, etc. This treater also consists of three chamber units, made up of three pairs of lead chambers. A lead-lined tower is placed between the first two pairs, in which the gas is scrubbed with water to remove chlorine and also fluorine if present. The gases pass from the treater to drying towers, where they are sprayed with concentrated sulphuric acid. The cleaned dry gas is then compressed by a rotary blower to a pressure of 1000 to 1200 mm. of water and delivered to the convertors. From an initial pressure of −180 mm. to the delivered pressure requires about 120 hp. with a capacity of 260 cu. m. per minute.

The contact apparatus consists of two systems of two convertors each, with a daily output of 45 tons of monohydrate per convertor, so that the normal daily output of the plant is 180 tons of monohydrate. Each convertor has six grids, two in the first stage and four in the second, on which the vanadium contact mass is spread. The conversion is about 80 to 82 per cent in the first stage and 16 to 18 per cent in the second, the total being 98 to 98.5 per cent. The convertor walls are cooled and this, together with the possibility of admixing cold gas, makes it possible to regulate the temperatures of the stages and grids very carefully. Each convertor has three heat exchangers, one of which lies between the first and second stage. Because of these precautions and careful insulation of the convertors and heat exchangers, it has not been necessary to heat the gases except when the convertors are being started up, in spite of the fact that gas with a concentration of 4 per cent SO_2 by volume, or even less, must often be treated for a long time when starting, and that interruptions of as much as 12 hr. sometimes have occurred.

The SO_3 gas from the heat exchangers is recovered as monohydrate or 20 to 35 per cent oleum by absorption in highly concentrated sulphuric acid, without previous cooling. Each of the two contact systems has a monohydrate tower and a fuming-acid tower, the first having a capacity of 90 tons of monohydrate per day and the second of 150 tons of 20 per cent fuming acid. In order to meet any market demands, apparatus is also provided in which the monohydrate can be diluted with water to any desired concentration.

The exit gases with traces of SO_3 are discharged to the air through a 100-m. chimney. In order to have a gas at all times harmless to vegetation when it leaves the chimney, this is so constructed that enough fresh air is drawn in to dilute the gas four to five times. This measure appeared necessary to avoid injury to vegetation of a very fertile agricultural region, such as that surrounding the works.

Zinc-leaching Plant

The calcine, containing 72 to 73 per cent Zn, is subjected in the leaching plant to a two-stage leaching process. Batch leaching was chosen for better control of operation and lower power consumption. Two-stage leaching gives a higher yield of zinc and, also, weakly acid residues may be filtered better than neutral residues. Cylindrical tanks of 100-cu. m.

useful capacity, with conical bottoms and lined with sheet lead and acid-proof brick, are used as the leaching tanks. The agitation is done by a propeller agitator made by the Maschinenfabrik-Augsburg-Nüremberg (Figs. 3 and 4), which agitates the pulp vertically, discharging it through a comparatively small tube. Its advantages over paddles are better mixing with less power consumption, less space required and equal operating and construction costs. The construction is of rubber-covered steel.

The neutral residue is separated from the zinc sulphate solution in thickeners 18 m. in diameter and 4 m. deep, with a total capacity of about 1100 cu. m. each. The thickened slime, containing about 450 grams of solids per liter, is pumped to a wet ball mill by a diaphragm pump and, after being ground to below 0.25, is leached with dilute sulphuric acid in a tank similar to the ones used for neutral leaching. The acid pulp is clarified in a thickener lined with lead, having rubber-covered rakes. The thickened acid pulp, containing 400 to 500 grams solids per liter, is filtered in Sauerbrey-Jung pressure filters. These filters are made up of rings of porous stoneware, hung on rubber-covered iron pipes to form a tube about 2 m. long. These tubes are suspended in a pressure tank, the core being the outlet for the filtrate. The vessel is filled with the pulp and kept under 7 atmospheres of pressure until the filtration is complete. The cake is washed with water and blown off with compressed air. In this way a residue containing about 20 to 25 per cent moisture is obtained, which, after being dried in a rotary furnace, is treated in the residue plant

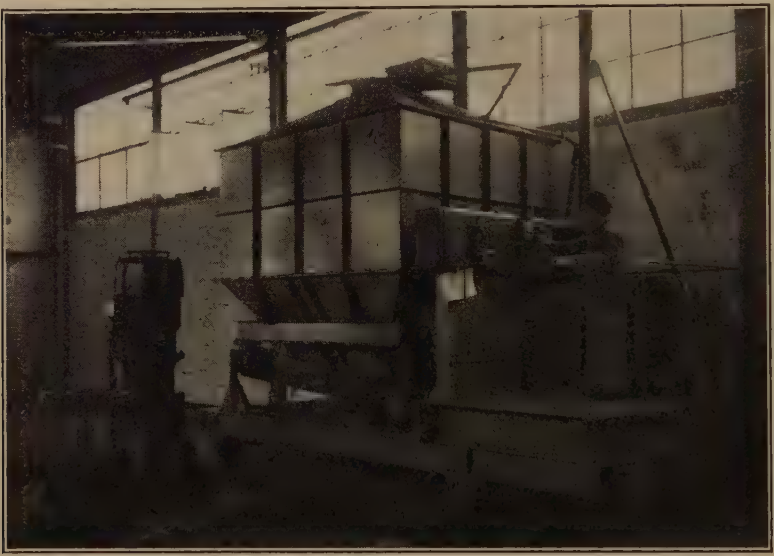


FIG. 3.—ZINC LEACHING. LORRY AT RIGHT, AGITATOR AT LEFT.

for recovery of the lead and zinc. With a daily residue production equal to 10 to 12 per cent of the calcine used for leaching, it contains 20 to 30 per cent Zn and 4 to 6 per cent Pb.

The zinc sulphate solution from the neutral thickener is purified in the usual way by blue powder, with an addition of copper sulphate if necessary. Filter presses are used to separate the purified solution from the precipitated metals, as is usual elsewhere. Consumption of zinc dust amounts to 1 per cent of the cathode zinc production. The residues, containing up to 35 per cent Zn, 12 per cent Cd and 2.5 per cent Cu, are treated in the cadmium plant. The purified sulphate solution is cooled to 25° to 30° C. in order to precipitate the $CaSO_4$, $MgSO_4$, SiO_2 and basic

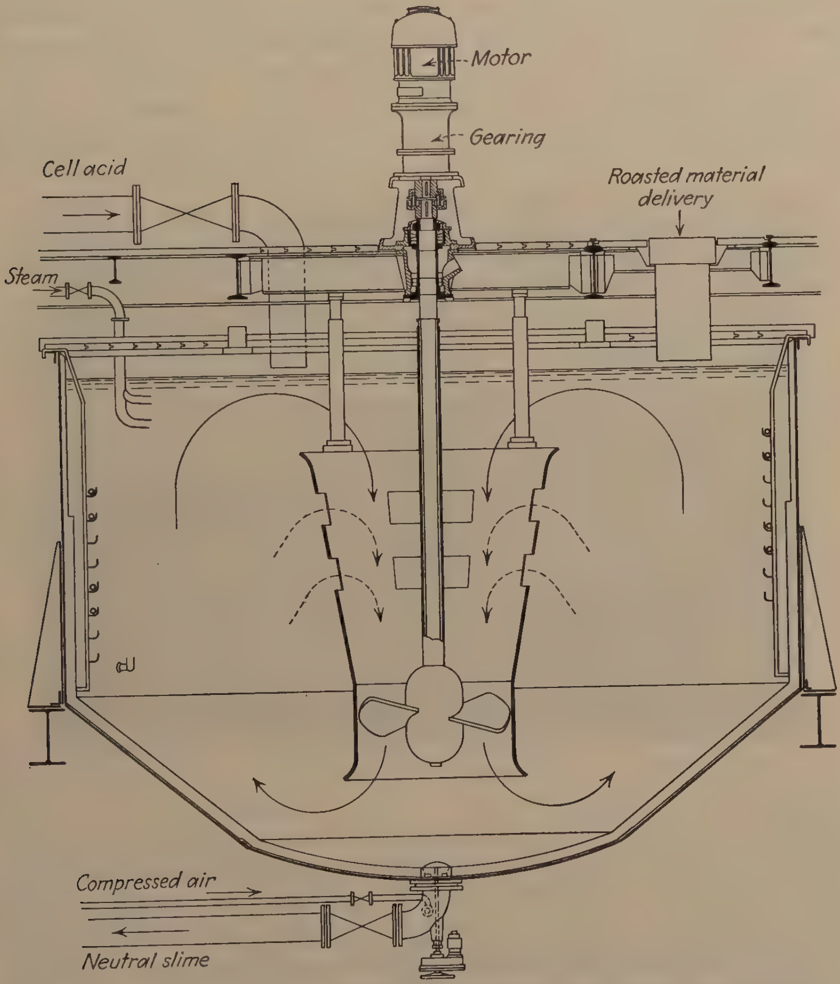


FIG. 4.—ZINC LEACHING. AGITATOR WITH M.A.N. SCREW PROPELLER.

zinc salts in solution. After this treatment it is pumped into storage tanks for electrolysis.

Zinc Electrolysis

The electrolyzing process was developed by lengthy experimentation with full-sized units. The operation and cell arrangement are described in U. S. Patent 1984745. Of the 480 cells, with internal dimensions 940 mm. width, 1400 mm. length and 1460 mm. (1360 useful) depth, 448 are normally in use and 32 in reserve. Cells and anodes are cleaned every six to eight weeks in rotation. Each cell contains 12 cathodes with depositing surfaces 600 by 960 mm. and 13 anodes with useful surfaces 580 by 945 mm. each, with a spacing of 23 mm. from cathode to anode. With a current load of 10,000 amp. per cell, the current density is 725 to 740 amp. per sq. m., depending upon the level of the electrolyte in the cell. The cells are made of reinforced concrete with a lining of sheet lead, 3 mm. thick, over an acid-resistant varnish. The 480 cells are placed in 30 rows of 16 cells each and are on one level (Fig. 5). A cell unit consists of 240 cells, so that there are only two groups. The immersed part of the anodes is perforated. They are made of a silver-lead alloy containing 1 per cent Ag. The cathodes are aluminum sheets, 5 mm. thick. For avoiding sprouts, the edges are protected by rubber strips, which have proved more satisfactory than wooden ones during almost two years of use, and have not yet required renewal.

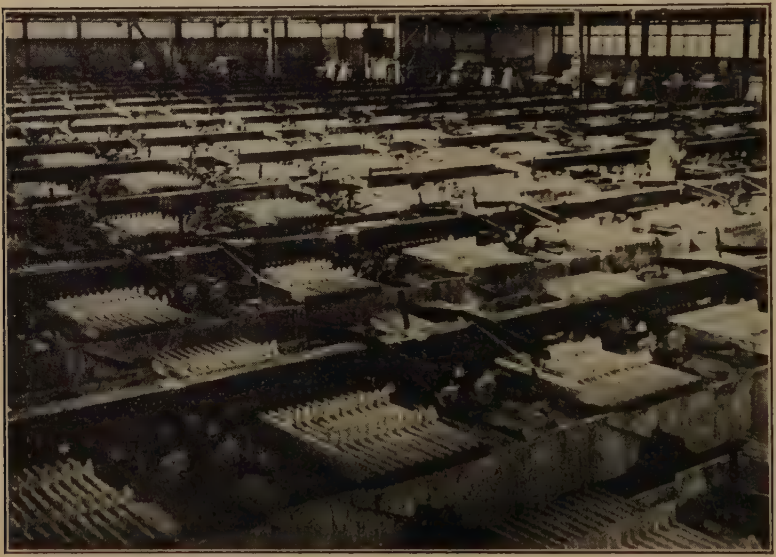


Fig. 5.—Tank room.

In contrast to the usual process of electrolysis, the concentration of the electrolyte in the cells is kept nearly constant at about 55 to 60 grams Zn and 150 to 160 grams free acid per liter. The neutral electrolyte, containing 160 grams Zn per liter, is led into the cells by siphons from a trough above the center of each double row of cells, and 100 to 105 grams Zn per liter is removed during electrolysis. The manganese content of the electrolyte is 2.0 to 3 grams per liter. The cell voltage fluctuates between 3.1 and 3.35 volts, dependent on the coating of manganese on the anodes.

The condition for good current efficiency is a constant concentration of zinc and acid in the electrolyte. With greater current density and smaller spacing between electrodes, however, this requirement cannot be satisfied without the use of special aids. At the Magdeburg plant, one means of attaining a constant electrolyte composition was worked out and patented (U. S. Patent 1984745). This was to close the side openings between the electrodes so that the evolution of gas and heat effected a positive and thorough circulation of the electrolyte, thus giving the desired uniform electrolyte composition.

The zinc cathodes are stripped every 24 hr., at present during the morning shift. For this purpose four cathodes are lifted at once and carried to the stripping room by a trolley rail. One man cares for a row of 16 cells and normally spends 5 to 6 hr. in lifting and stripping the cathodes, cleaning their contacts and replacing them.

A temperature of 35° to 40° C. is maintained by water-cooled lead coils (Fig. 6) placed at the ends of the cell. About 60 mg. of glue per liter of neutral electrolyte, or 350 to 400 grams per ton of cathode zinc, is added to the cell.

TRANSFORMING AND RECTIFYING PLANT

Large iron-cased mercury-vapor rectifiers are used to provide the direct current for the electrolysis. As this alone consumes about 125,000,000 kw-hr. per annum, any improvement in efficiency has an importance not to be underestimated, in view of the large part played by current in the cost of making electrolytic zinc. It was known that a high conversion efficiency could be obtained with large rectifiers working at higher voltages than are usual in zinc-electrolyzing plants. It was therefore decided to divide the 480 cells into two groups of 240 cells each, which called for a voltage of 750 to 850 volts on the direct-current side of the rectifier. The conversion efficiencies given for these voltages by the manufacturers were 94.5 per cent for rectifiers and 93 per cent for rotary convertors. Another fact in favor of the rectifier is that, having no moving parts, it requires little attendance, and that its cost is considerably less than that of the rotary convertor. All expectations have been fully confirmed by two years of operation.

By an especially exact method of measurement the conversion efficiency has been found to be 95 per cent. The high voltage of 750 to 850 volts for one cell group is especially noteworthy. So far as is known, it is used here for this purpose for the first time. By means of a special wiring scheme (Fig. 7) and very carefully installed insulation, which, of course, is necessary at any rate, safety in maintenance and operation is attained.

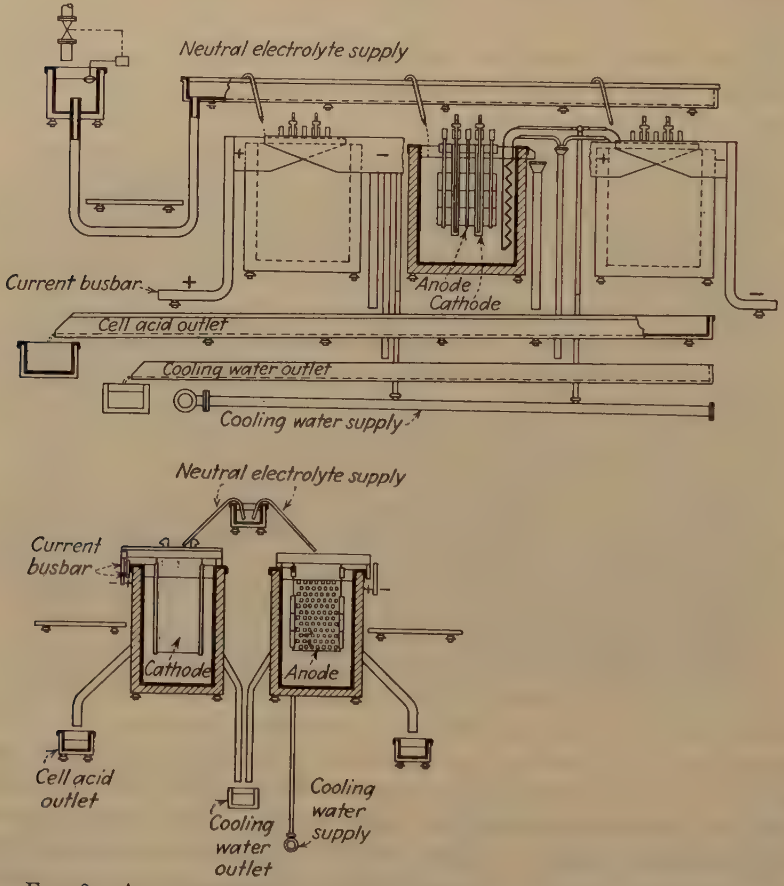


FIG. 6.—ARRANGEMENT AND CROSS SECTION OF ELECTROLYTIC CELLS.

Each cell group has a rectifier group; another rectifier group stands in reserve. Each consists, in addition to the usual high-tension apparatus, of the special 10,000-kva. transformer with six-phase winding, the reaction coil and two 5000-amp. rectifiers, which deliver, connected in parallel, 10,000 amp. between 715 and 820 volts. The rectifier anodes are grid-controlled. This permits the direct-current voltage to be regulated by steps from 0 to 820 volts, the load to be taken up in the same way.

Grid control gives the same ease of regulation to the rectifier that the motor generator has. It has the further advantage of affording the best protection against short circuits within and without the rectifier. In cases of short-circuiting, the affected group of cells is cut out in less than $1/50$ sec. by the automatic switches, and at the same time all the anode grids are put on negative voltage, so that there is no charging current. When the short circuit is removed, the affected cell groups are reconnected automatically, so that the electrolytic process is unaffected. The 10,000-amp. direct current produced reaches both cell groups through a switch and distribution system constructed entirely of aluminum. With this distribution system and the aid of grid control, it is possible to transfer the load from either rectifier to the reserve rectifier gradually and evenly.

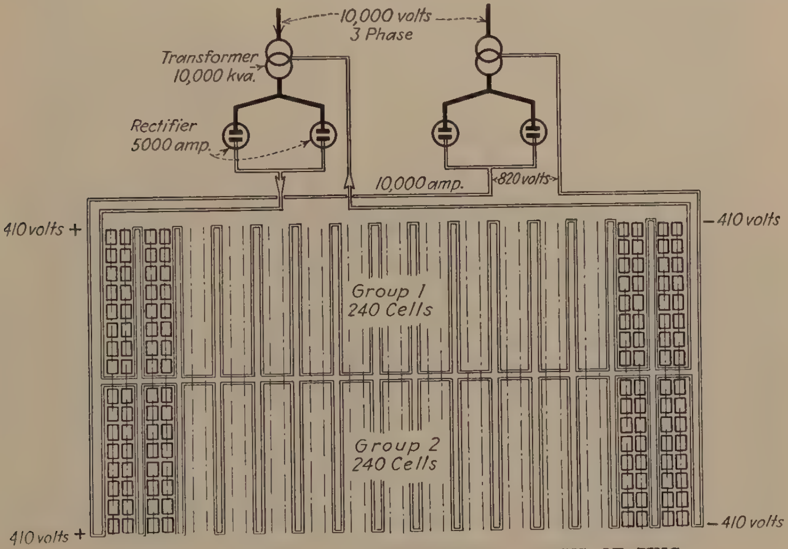


Fig. 7.—Wiring scheme for electrolysis of zinc.

Melting Plant

The unwashed zinc cathodes are stacked on racks as they are stripped. After weighing, they are trammed to the melting furnaces by storage-battery trucks. Here they are lifted from the racks to the charging chute by electric cranes with hand-operated chain control. The furnaces are fed by hand. Low-frequency induction furnaces with a capacity of 20 and 10 tons of molten zinc and a melting capacity of 3 and 2 tons per hour, respectively, are used (Fig. 8). They are the first to be made of these sizes. The two larger furnaces have a connected load of 550 kva. and were built by the Siemens and Halske A.-G., Berlin. The 2-ton furnace has a connected load of 350 kva., and was supplied by the A.E.G., Berlin. The power consumption is 110 kw-hr. per ton of slab zinc.

As the zinc cathodes are charged and melted, zinc is ladled out through a ladling door with 120-kg. pouring ladles and cast in iron molds into the usual commercial slabs weighing about 20 kg. Seventy-five slabs at a time are piled on a low rack and taken by a specially constructed tiering truck to the storehouse or direct to loading.

Melting is facilitated by the addition of about 400 grams sal ammoniac per ton of slab zinc. Of the cathode zinc melted, 97.5 per cent is recovered as slab zinc and only 2.5 per cent is converted into dross containing about 85 per cent Zn. This contains about 1 per cent chlorine, from the sal ammoniac. After being dechloridized by calcining in a short rotary kiln, it is leached in the usual way.

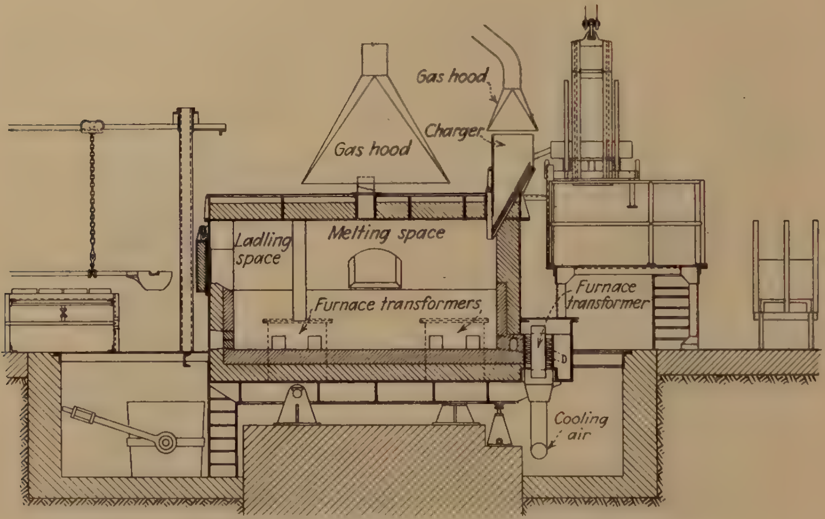


FIG. 8.—ELECTRIC FURNACE FOR MELTING ZINC CATHODES.

CADMIUM PLANT

The cadmium precipitates from the zinc leaching, containing about 35 per cent Zn, 2.5 Cu, 2.5 per cent Pb, 0.04 per cent Ni, 0.005 per cent Co and 0.15 per cent As, with up to 12 per cent Cd, are treated for electrolytic cadmium. The zinc is recovered by leaching as a zinc sulphate solution, which is delivered to the zinc-leaching plant. In developing the process, special emphasis was placed upon removing the nickel, cobalt and arsenic as completely as possible from the cycle. This can be done by treating the zinc-cadmium residues with zinc-cell acid directly after wet grinding, without any preliminary drying and roasting. The acid is added gradually to the suspension obtained in the wet grinding.

In this method of treatment a certain excess of metallic zinc or cadmium is constantly present, so that any copper, nickel or cobalt that dissolves is reprecipitated immediately.

The danger from arsine is taken into account, of course. To prevent any such poisoning, each solution tank is covered, and care is taken to exhaust the gases and dilute them sufficiently with fresh air. In addition, good ventilation is provided for the leaching plant. These measures have proved fully satisfactory.

By filtering in presses a copper residue is produced together with a zinc-cadmium solution with about 20 to 30 grams per liter of cadmium. The cadmium in the filtrate is precipitated as cement cadmium containing about 80 per cent Cd, by gradually admixing blue powder. The cement cadmium is dissolved in cell acid from the cadmium electrolysis, without any preliminary treatment. The resulting $CdSO_4$ solution is purified from such constituents as cobalt, iron, thallium, etc., and then passes into the cadmium electrolysis with a content of 180 to 200 grams Cd, 20 to 30 grams Zn, 0.5 grams Mn and 40 to 50 mg. Ni per liter.

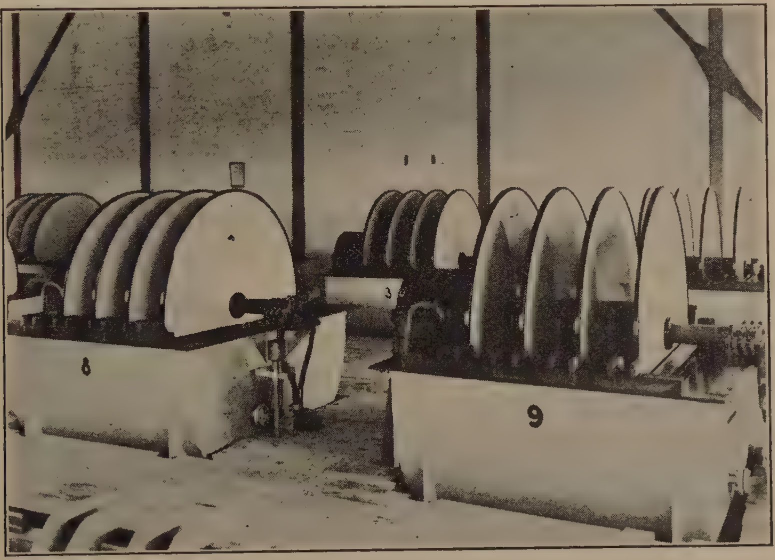


FIG. 9.—ELECTROLYSIS OF CADMIUM.

The cells have a semicircular cross section, are made of sheet iron and are rubber-lined (Fig. 9). Each cell contains four aluminum cathodes, 1420-mm. dia. and 8 mm. thick, which are placed, for easy handling, 250 mm. apart on a steel shaft. Two lead anodes, shaped like segments of a circle, serve each cathode. The spacing between anode and cathode is 36 mm. Each cell has its own inlet and outlet for electrolyte, so that the concentration rates can be kept approximately constant, these being at present 20 grams Cd and 140 grams free H_2SO_4 per liter. By using rotating cathodes, practically sproutless deposits are obtained, which are removed every four days as a rule.

The direct current required is supplied by a motor generator. The current density is 250 amp. per sq. m. and the cell voltage 2.65 to 2.7 volts.

The cadmium cathodes are melted in a tilting electric crucible furnace under a layer of charcoal. The cadmium dross produced amounts to 2.5 to 3 per cent of the charge. The contents of the furnace are cast by hand into the usual commercial shapes, pencils, cakes and slabs.

The production of the plant corresponds to the cadmium in the flotation blende worked, and amounts to 150 to 180 tons per year.

The precipitated residues from the leaching contain up to 25 per cent Cu, the average being 15 per cent.

Residue Plant

The problem of the residue plant is to work up the zinc and lead residues from the zinc-leaching plant into oxide, remove the chlorine and lead from this oxide and from the roaster-flue dusts, to remove chlorine from the dross, and, finally, to work these leady intermediate products into work lead.

For this purpose three short rotary kilns are provided for batch treatment, as proposed by Dörschel for these and similar processes. Each is 7650 mm. long and 2600 mm. external diameter. One furnace is used to remove chlorine and lead, and the other two are normally engaged in working up the leaching-plant residue. As necessary, lead smelting is done in one of the last two furnaces.

Heating of these furnaces is by pulverized coal, which is ground on the spot. A movable port connects the furnace to the waste-gas flue. The waste gases, after leaving the furnace, first pass through a cyclone and then through a countercurrent gas cooler. After cooling to between 100° and 120° C., they enter a baghouse having mechanically shaken woolen bags through which the gas is filtered. The oxide recovered here is carried by a pneumatic conveyor to the place of further treatment.

The daily production of leaching-plant residue, amounting to about 25 dry tons of material containing 25 per cent Zn, 6 per cent Pb, 0.4 per cent Cd, 20 to 25 per cent Fe, 9 to 11 per cent total S, 400 grams per ton Ag and 7 to 10 per cent moisture, is delivered to the furnace in charges of about 6 tons, with about 20 per cent coke breeze. After volatilization of the zinc and lead, the molten charge is dumped into trough-shaped slag cars, where the matte, containing 65 per cent Fe, 20 per cent S and about 1800 grams Ag per ton, is separated from the slag. The slag proper contains 3 to 4 per cent Zn and 40 per cent Fe. Slag and matte amount to about 50 per cent of the dry residues smelted.

YIELD OF METAL

The re-treatment of all the intermediate products of the plant makes it possible to obtain a recovery of 98 to 99 per cent of the zinc in the ore as slab zinc. From 90 to 95 per cent of the cadmium in the ore is recovered as electrolytic cadmium.

Recovery as work lead of the lead that is present is now being investigated on a commercial scale, and results indicate this to be possible with the existing equipment. Owing to the short period of experimentation, however, a detailed description is not yet possible.

The copper in the flotation blende, which comes almost entirely from the flotation reagents, is concentrated up to an average of 15 per cent Cu in the residues from the cadmium plant. Experiments for its recovery in a commercial form are still under way.

Silver is recovered in a matte, which so far has not been treated. The matte is sold to lead smelters, where it is used as a flux in smelting lead and the silver is thus recovered.

ECONOMICS

The power consumption in the zinc-producing operations of roasting, leaching, electrolysis and melting is about 3600 kw-hr. per ton of slab zinc. This makes up about 60 per cent of the operating cost.

Including technical and office employees, 810 men are employed, 110 of whom are in the sulphuric acid, cadmium and residue plants. About 10 per cent of the workmen are always absent because of illness or holidays; 30 men are engaged in the apprentice shop and 10 in welfare work.

The cost of zinc production may be said in general to be within the cost limits of other electrolytic plants, in spite of the cost of electric current, which is relatively higher than in other countries.

CONCLUSION

It is obviously impossible, within the limits of this article, to go more fully into details of construction, or to describe all the details of operation, questions of materials, machinery and apparatus. All that can be given is a sketch of the history of the works, essential data of its design, peculiarities of the process and equipment in use, with some characteristic details of the operations.

It may be said that Georg von Giesche's Erben, by building and operating the Magdeburg zinc works, has again become the most important zinc producer in Germany. With a yearly output of 40,000 tons of electrolytic zinc, heretofore not produced in Germany on a commercial scale, it almost meets the German demand for high-grade zinc.

Electrolytic Zinc at Risdon, Tasmania

By W. C. Snow*

The plant of the Electrolytic Zinc Company of Australasia Limited, situated at Risdon on the estuary of the River Derwent, near Hobart, was designed and erected primarily to produce high-grade zinc from zinc concentrates produced by the mines of Broken Hill, N. S. W. Consequently the metallurgy of the process has been influenced in its development by the peculiar characteristics of the Broken Hill concentrate, which on treatment gives into solution relatively large amounts of cobalt, manganese and silica.

The Risdon works (Fig. 1) produces high-grade electrolytic zinc, leaded electrolytic zinc, zinc dust, cadmium, sulphuric acid and superphosphate. This paper, however, is concerned only with the zinc plant and process.

ROASTING

The roasting of raw concentrate is not a major feature of Risdon's process, and in this respect practice is unlike that of most zinc plants. The roasting is mostly done on the Australian mainland at centers where the sulphuric acid made from the roaster gases can be used for superphosphate manufacture. A small amount, approximately 40 tons† per day, is roasted at Risdon, acid being manufactured from the gases. The amount that can be roasted there is limited by the acid requirements of the zinc plant and of the superphosphate plant. Roasting is not carried to completion at the mainland plants, and the product, known as preroast calcine, largely constitutes the raw material for the Risdon zinc plant. It contains about 6 per cent of sulphur as sulphide. Roasting is completed at Risdon for reasons that are set out later in this paper.

The zinc plant proper is divided into four main divisions: (1) final roasting division, (2) leaching and purification division, (3) electrolytic division, (4) melting and casting division. There are two subsidiary divisions—the cadmium division and the preroast, acid and superphosphate division.

Manuscript received at the office of the Institute Aug. 17, 1936.

* Plant Superintendent, Electrolytic Zinc Company of Australasia Ltd., Hobart, Tasmania.

† Throughout this paper the ton is 2240 lb. and the gallon is the Imperial gallon.

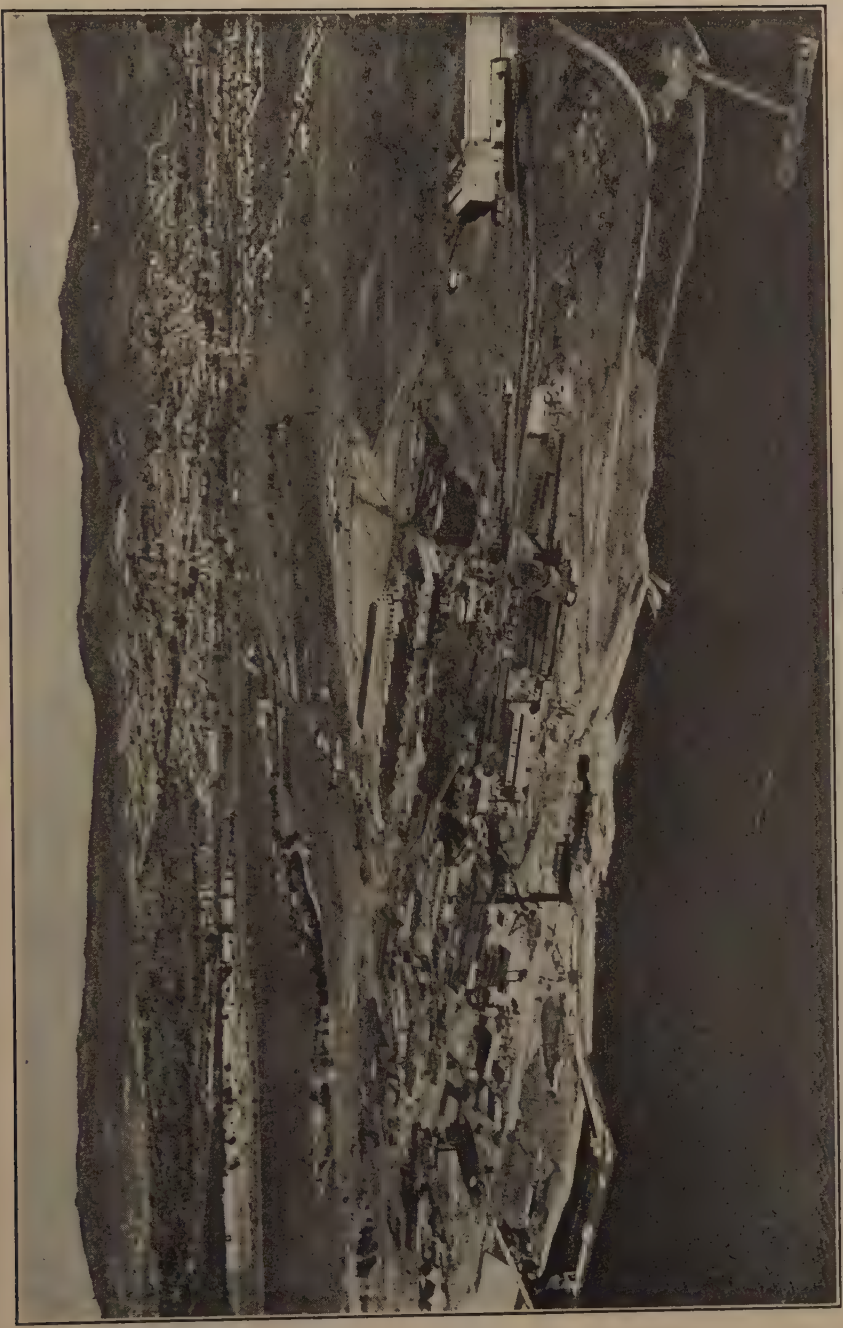


FIG. 1.—GENERAL VIEW OF RISDON WORKS.

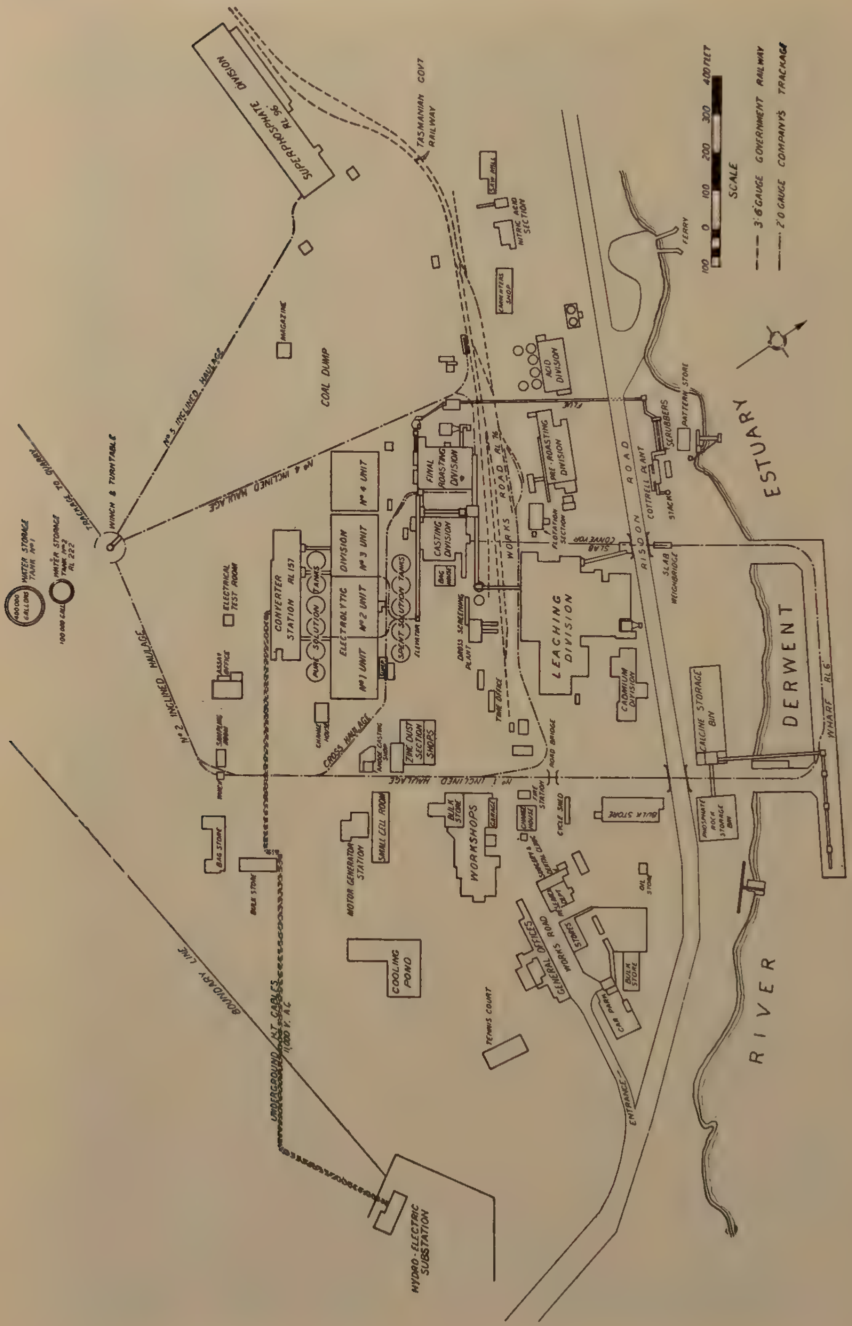


FIG. 2.—GENERAL PLAN OF RISDON WORKS.

Servicing these plants are handling and storage arrangements, power supply, repair shops and assay and research laboratories. Fig. 2 is a general plan of the works.

Raw materials (preroast calcines, raw concentrates and phosphate rock) are received at the wharf front in cargoes of 4000 to 4500 tons.

Coal comes by rail from collieries in the northeastern part of Tasmania; it has a calorific value of 9,500 to 10,000 B.t.u.

The capacity of the foreshore storage bin is approximately 20,000 tons of calcine. The calcine discharges onto a 3 by 8-ft. Jacques vibrating screen set at an angle of 35° from the horizontal. The screen mesh is ⅝ by ⅝ in. at the upper end and ½ by ¾ in. at the lower end. Oversize from the screen passes through a hammer-type disintegrator and back to the boot of the elevator. Undersize from the screen falls onto an 18-in. belt conveyor and by means of a tripper is spread over two storage bins, each of 390 tons capacity.

Dross from the melting plant and flue dust from the roasting furnaces are also delivered to these bins and with the preroast calcine form the furnace charge, which is delivered through bottom-discharge chutes controlled by horizontal and vertical gates onto four 18-in. belt feeders delivering to the top hearths of four furnaces. Fig. 3 is a plan of the furnace layout with connecting flues and discharge conveyors.

The furnaces (Fig. 4) are of Risdon design and are a modification of the Leggo furnace as used for roasting arsenical pyrite. Each furnace has four superimposed hearths 85 by 8 ft., giving a total hearth area of 2720 sq. ft. or a rabbled area of approximately 2200 sq. ft. These furnaces have been in practically continuous operation since 1922 and no complete hearth replacements have yet been necessary.

Each hearth of each furnace has a short flue fitted with a damper, connecting it with the main flue system. A 100,000-cu.ft. fan drafts all furnaces. The furnace charge is fed onto the top hearth through a hole in the arch and from this hearth to the intermediate and bottom hearths through openings regulated by slides. Ideally each hearth is a separate furnace and originally was fed separately with a screw from a hopper at the side of the furnace, but because of packing of material in the hopper and in the screws, satisfactory regulation of feed was impossible and the present scheme was resorted to.

Because of inevitable air leaks around the furnace columns, the upper hearths tend to be hotter than the lower ones and the distribution of draft and feed is designed to minimize and compensate these differences so far as possible. The object of this final roasting operation is fourfold:

1. To oxidize zinc sulphide, forming zinc oxide. The preroasting operation, which is carried out without extraneous fuel and which is required to produce a gas reasonably high in sulphur dioxide content for

acid making, yields a preroast calcine which contains 7 to 7.5 per cent of total sulphur, 1 to 1.5 per cent sulphate sulphur and about 6 per cent sulphide sulphur. With each final roasting furnace treating 90 tons of charge per day, with a fuel consumption of 10 to 12 per cent of the weight of the charge, the sulphide sulphur is reduced to about 0.8 per cent.

2. To eliminate chlorine. The preroast calcine produced at the various roasting plants is wetted to prevent dusting during handling, storage and transport. The water used is relatively high in chlorine. Since the material is sea-borne to Risdon it is liable to accidental wetting with sea water. The final roasting operation eliminates 92 per cent of the chlorine in the charge. The discharge from the furnaces contains 0.003 per cent chlorine, which enters solution and requires special provision for its removal; the procedure necessary is described in the section on purification. Dross from the melting plant, which forms part of the furnace charge, is rich in chlorine as a result of its treatment with ammonium chloride, and this by-product is included in the roaster charge. The removal of chlorine from the dross is more effectively done by roasting it together with a sulphide material, or in an atmosphere of SO_2, than by roasting it by itself.

3. To eliminate moisture. The moisture in the furnace charge amounts to about 8000 gal. per 24 hr. The evaporation of this water, which otherwise would enter the zinc circuit, is a useful function of this operation, enabling the use of a like amount in the washing of leach-plant residues.

4. Control of sulphate formation. This is now a matter of minor importance, but in the early days of the plant was a major feature of the final roasting. The material reaches roasting temperature by the time it has traversed about one-third of the length of the hearth; at the middle portion it is approximately 650° C. and at the discharge end 750° to 800° C.

The temperature is maintained by the combustion of slack coal on a traveling grate stoker. Each stoker (one per furnace) has a grate area of 45 sq. ft. and burns 9 to 10 tons of Tasmanian slack coal per day. The coal has a thermal value of 9500 B.t.u. and contains about 24 per cent ash and 51 per cent fixed carbon. Ash drops into a pit under the end of the stoker and is removed by a drag chain conveyor serving the four furnaces. Each stoker has its separate blast fan delivering 5000 to 6000 cu. ft. of air per minute. The air is preheated to 70° to 80° C. by being drawn through the furnace columns and from hot conveyor housings.

The hot calcine discharges from the side of each furnace into a steel push conveyor running parallel with the side of the furnace. Each conveyor is 52 ft. long, with 18-in. blades spaced at 12-in. intervals, working at about twenty 18-in. strokes per min. These four conveyors

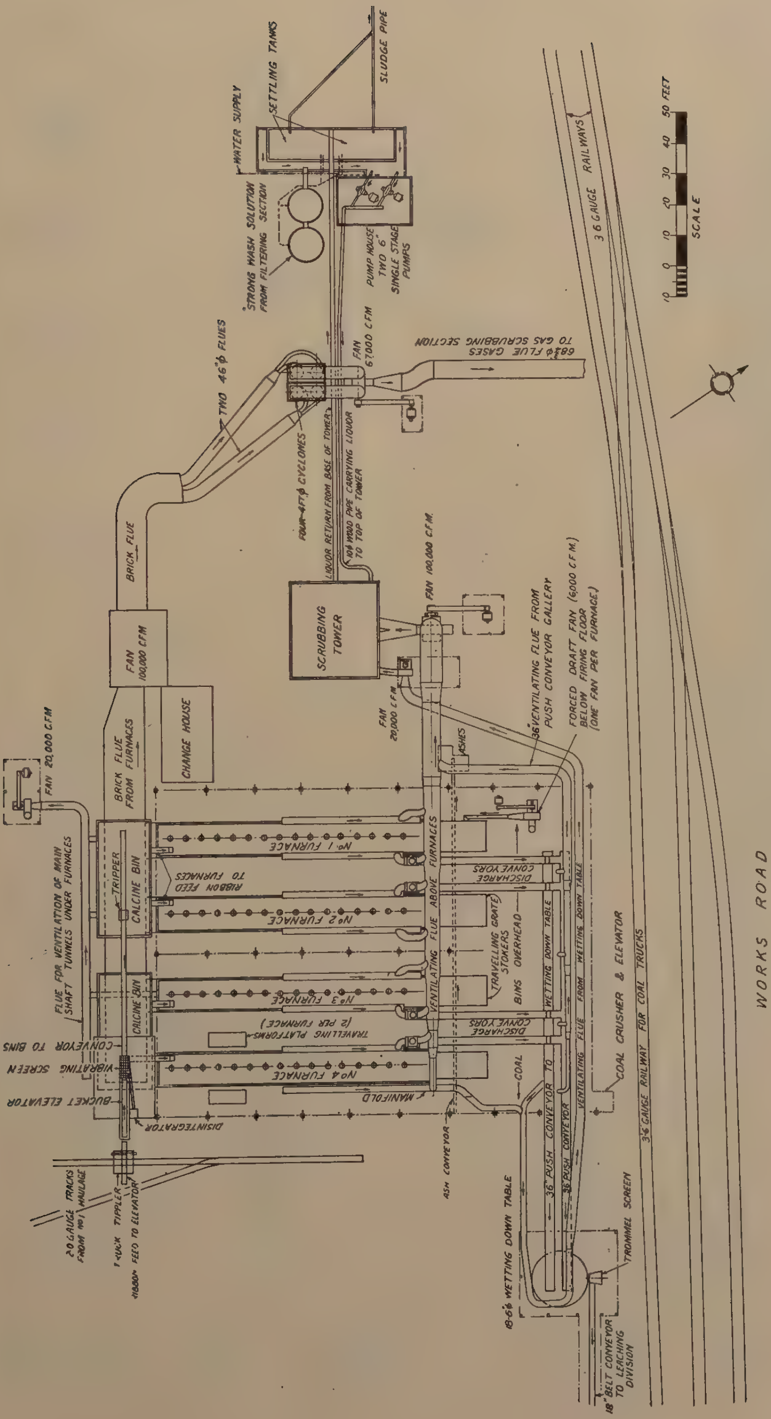


FIG. 3.—GENERAL PLAN OF FINAL ROASTING DIVISION.

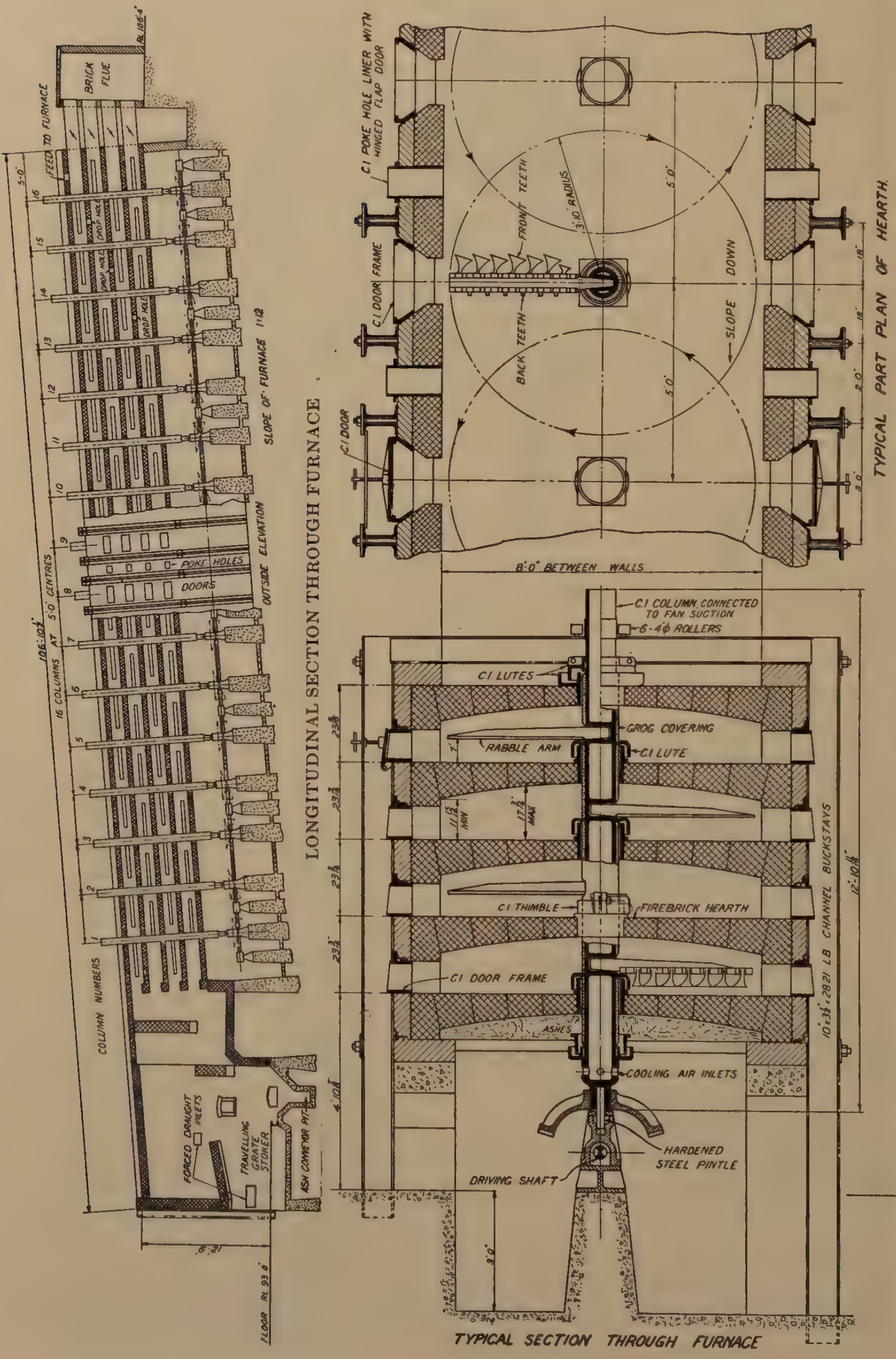


FIG. 4.—SECTIONAL VIEWS OF FINAL ROASTING FURNACE.

discharge into two 36-in. push conveyors. The push conveyor, but little known or used elsewhere, while somewhat cumbersome, has proved to be a satisfactory machine for conveying and cooling the hot calcine with a minimum of dusting.

Delivery from the 36-in. conveyors is onto the center of an 18-ft. 6-in. circular revolving table above which are suspended fixed blades, which work the material from the center to the periphery. By the time it reaches the table the calcine is sufficiently cooled to permit of wetting to prevent dusting in further handling. The wetting is done by spraying the calcine on the revolving table with strong wash (weak zinc) solution from the filters in the leaching division.

From the periphery of the wetting-down table the moistened calcine drops into a conical trommel screen of ½-in. mesh, the undersize falling onto an 18-in. inclined belt-conveyor system delivering into a 50-ton storage bin in the top of the leaching building. Oversize from the screen is returned to the furnaces after passing through the disintegrator.

The most serious difficulty in roasting arises from the pronounced tendency of the material to form hard cakes on the hearths, in the dead areas against the furnace walls, and on the rabble teeth. The work of the furnacemen is chiefly devoted to the prevention of caking by slicing the hearths, particularly the dead-area portions, to removing cakes that have formed and to keeping the rabble teeth and discharge chutes free of lumps and accretions. The hot half of each hearth has to be sliced every 24 hr., the next quarter every 48 hr., while the feed end requires slicing only once a week. Traveling platforms are provided for working the upper hearths. The furnaces with flat hearths are much easier for furnacemen to keep clean and hearth replacements when necessary will be of this type. The necessity for such frequent slicing is a serious disadvantage in the proper control of draft and temperature and is also the cause of dust and gas escaping into the furnace room, particularly from the pressure ends of the furnaces. To take care of this a dust-collecting and ventilating system is installed. The two fans of this system discharge their gases into a scrubbing tower where practically complete recovery of the dust and the SO_2 is made, the sensible heat of the gases is also utilized in the concentration of weak zinc solutions.

The tower is indicated in Fig. 3. It is irrigated with strong wash solution (30 to 40 grams zinc per liter) from the leaching division at the rate of 1200 gal. (Imperial) per minute. The effluent passes to two 20 by 10-ft. concrete settling ponds, the overflow from which is returned to the top of the tower by two single-stage 6-in. bronze pumps. This solution quickly increases in zinc concentration, the warm gases accounting for the evaporation of about 12,000 gal. of water per day. Once each week the tower is opened and the launders and lower splashboards cleaned, and once a year the whole packing is removed and freed from accretions of gypsum and basic zinc sulphate.

A large excess of air is used in the furnaces and the roast is a strongly oxidizing one. The gas contains 0.5 to 0.75 per cent SO_2, about 15 tons of calcine dust daily, small amounts of SO_3 and of chlorine probably in the form of ammonium chloride and zinc ammonium chloride. Over 90 per cent of the dust is recovered by a cyclone system. All of the remaining dust, 80 to 90 per cent of the SO_2, and nearly all of the chlorine

TABLE 1.—*Typical Metallurgical and Operating Data of Roasting Division*

AVERAGES FOR FOUR-WEEKLY PERIOD FOR YEAR 1934–35

	Tons	Assay, Per Cent Zinc
Feed to furnaces:		
Preroast calcines	9074	56.4
Zinc concentrates	177	52.6
Zinc dross and flue dust	267	77.4

Total feed, 9518 = 84.97 tons per furnace per day.

Average assay:

Moisture, Per Cent	Ag, Oz. per Ton	Pb, Per Cent	Zn, Per Cent	Total S, Per Cent	Sulphate S, Per Cent	Sulphide S, Per Cent	Cl, Per Cent
10.3	2.3	1.6	57.3	7.53	1.27	6.26	0.042

Discharge:

Final roast calcines.................................... 9267 tons.

	Ag, Oz. per Ton	Pb, Per Cent	Zn, Per Cent	Total S, Per Cent	Sulphate S, Per Cent	Sulphide S, Per Cent	Cl, Per Cent
Average assay	2.2	1.65	59.1	2.02	1.19	0.83	0.003

Roasting loss............... Zinc, 0.30 per cent. Stoppages: 285 furnace hours.

Coal consumed.............. 1070 tons = 11.24 per cent of furnace feed.

Cyclone dust............... caught and returned to furnaces, 410 tons.

Rabble arms:

, Changed............... 32.

Discarded.............. 6, equivalent to 1672 tons roasted per rabble arm.

Rabble teeth discarded....... 117, equivalent to 81 tons roasted per rabble tooth.

Columns changed............ 1, equivalent to 8838 tons roasted per column.

Power consumption:	Hp		Hp-hr. per Ton Roasted
Furnace drives	27	=	0.130
Stoker drives	6.5	=	0.034
	33.5	=	0.164
Push conveyor drives	30	=	0.156

In cyclone and flue-system fans:

No. 1, 50 hp......... No. 1A, 108 hp. No. 2, 104 hp. No. 3, 53 hp.

Total............. 315 hp.

In scrubber-water pumps.. 163 hp.

are removed by scrubbing with salt river water, and practically all of the SO_3 is removed by a Cottrell precipitator, which discharges to a woodstave stack 120 ft. high. Twice each shift the treater is flushed with salt water to remove precipitated solids.

Typical metallurgical and operating data of the roasting division are given in Table 1.

LEACHING

It is not only in the two-stage roasting that Risdon practice departs from that of other large electrolytic-zinc plants. In leaching, the common practice is the two-stage (acid and neutral) countercurrent continuous leach. The residues from such a leach necessarily contain all those acid-soluble constituents of the calcine that are precipitated by neutralization with excess zinc oxide such as silica, iron, arsenic and antimony.

At Risdon a single-stage batch process is used and the leach is maintained acid. The insoluble residue is mostly separated from the acid solution before the above-mentioned elements are precipitated by neutralization, which is effected by means of finely ground limerock instead of excess calcine. It is not intended to argue the relative merits of the two practices. These will vary with local conditions and character of material treated. The Risdon practice was developed because of the presence of relatively large amounts of soluble silica in the calcine, which in neutral leaching caused serious difficulty in the subsequent filtering, washing and drying of the residue, and to an undesirable degree increased the bulk to be shipped a long distance to a lead smelter.

Following is an outline of the several stages involved in leaching and purification of the resultant leach liquors:

1. Leaching of calcine in spent acid solution.
2. Classification of the leach pulp to separate granular residue.
3. Treatment of granular residue, by grinding, flotation, and leaching to recover unroasted sulphides as a concentrate, and to extract additional soluble zinc.
4. Thickening of the pulp from items 2 and 3 to remove slime residue from the bulk of the solution, and prepare a pulp suitable for filtering.
5. Filtering, washing, drying and disposal of the slime residue.
6. Preparation of ground limerock pulp, and treatment of the clarified solution from item 4 therewith to effect the more or less complete precipitation of iron, arsenic, antimony, silica, etc.
7. Filtration of the limerock precipitate pulp; chemical treatment, and washing of the precipitate to reduce its zinc and silver content, and finally its disposal to waste.

8. Precipitation by zinc dust and removal from the solution of copper, cadmium, silver, etc. by filtration. The precipitate passes to the cadmium division.

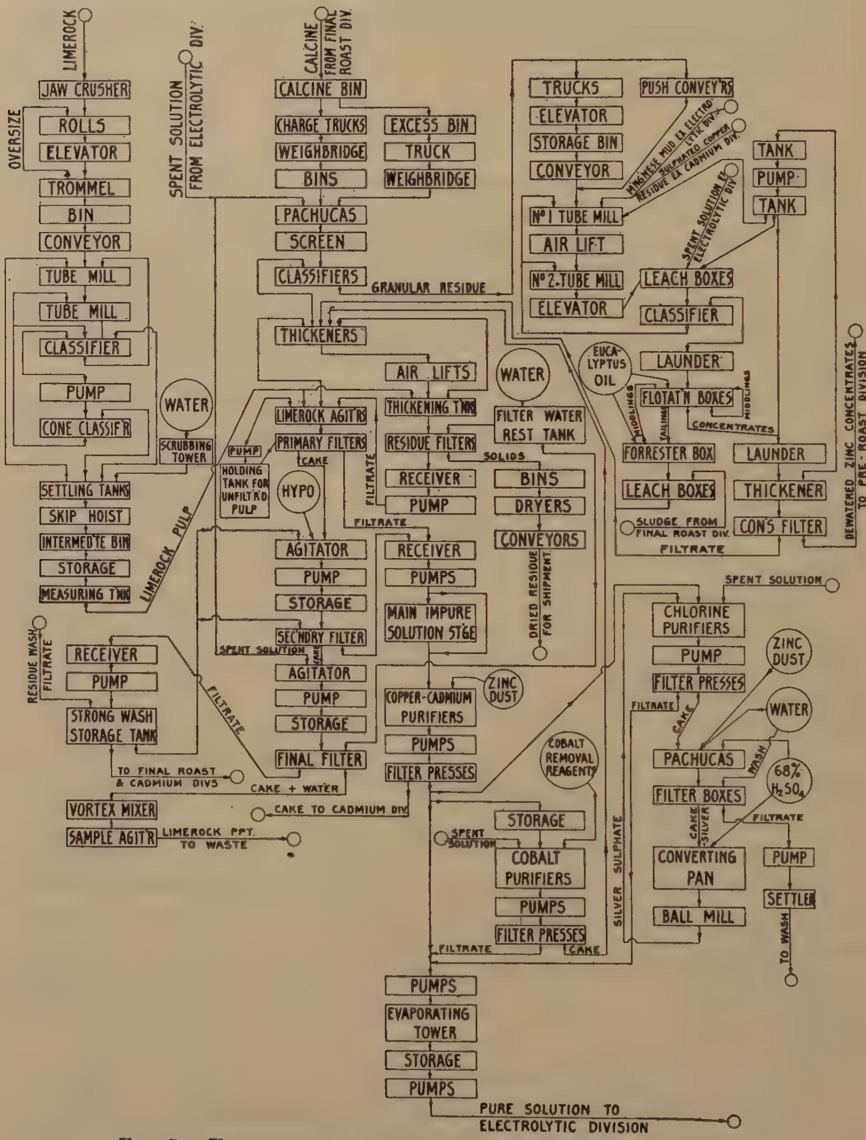
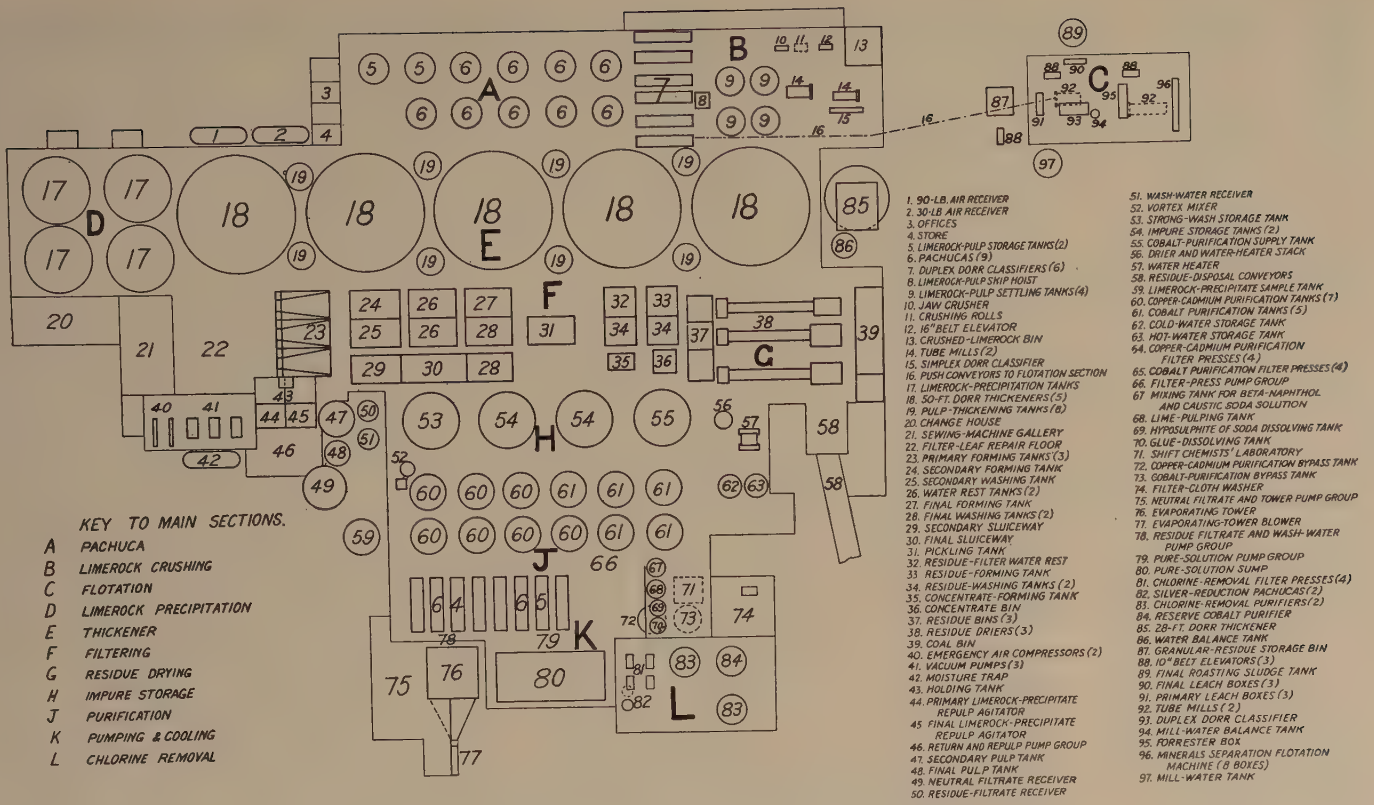


FIG. 5.—FLOWSHEET OF LEACHING AND PURIFICATION DIVISION.

9. Precipitation of cobalt by nitroso-beta-naphthol followed by filtration and disposal of precipitate. Only 55 to 60 per cent of the solution is so treated.



KEY TO MAIN SECTIONS.

A PACHUCA
B LIMEROCK CRUSHING
C FLOTATION
D LIMEROCK PRECIPITATION
E THICKENER
F FILTERING
G RESIDUE DRYING
H IMPURE STORAGE
J PURIFICATION
K PUMPING & COOLING
L CHLORINE REMOVAL

1. 90-LB. AIR RECEIVER
2. 30-LB AIR RECEIVER
3. OFFICES
4. STORE
5. LIMEROCK-PULP STORAGE TANKS (2)
6. PACHUCAS (9)
7. DUPLEX DORR CLASSIFIERS (6)
8. LIMEROCK-PULP SKIP HOIST
9. LIMEROCK-PULP SETTLING TANKS (4)
10. JAW CRUSHER
11. CRUSHING ROLLS
12. 16" BELT ELEVATOR
13. CRUSHED-LIMEROCK BIN
14. TUBE MILLS (2)
15. SIMPLEX DORR CLASSIFIER
16. PUSH CONVEYORS TO FLOTATION SECTION
17. LIMEROCK-PRECIPITATION TANKS
18. 50-FT. DORR THICKENERS (5)
19. PULP-THICKENING TANKS (8)
20. CHANGE HOUSE
21. SEWING-MACHINE GALLERY
22. FILTER-LEAF REPAIR FLOOR
23. PRIMARY FORMING TANKS (3)
24. SECONDARY FORMING TANK
25. SECONDARY WASHING TANK
26. WATER REST TANKS (2)
27. FINAL FORMING TANK
28. FINAL WASHING TANKS (2)
29. SECONDARY SLUICEWAY
30. FINAL SLUICEWAY
31. PICKLING TANK
32. RESIDUE-FILTER WATER REST
33 RESIDUE-FORMING TANK
34. RESIDUE-WASHING TANKS (2)
35. CONCENTRATE-FORMING TANK
36. CONCENTRATE BIN
37. RESIDUE BINS (3)
38. RESIDUE DRIERS (3)
39. COAL BIN
40. EMERGENCY AIR COMPRESSORS (2)
41. VACUUM PUMPS (3)
42. MOISTURE TRAP
43. HOLDING TANK
44. PRIMARY LIMEROCK-PRECIPITATE REPULP AGITATOR
45 FINAL LIMEROCK-PRECIPITATE REPULP AGITATOR
46. RETURN AND REPULP PUMP GROUP
47. SECONDARY PULP TANK
48. FINAL PULP TANK
49. NEUTRAL FILTRATE RECEIVER
50. RESIDUE-FILTRATE RECEIVER
51. WASH-WATER RECEIVER
52. VORTEX MIXER
53. STRONG-WASH STORAGE TANK
54. IMPURE STORAGE TANKS (2)
55. COBALT-PURIFICATION SUPPLY TANK
56. DRIER AND WATER-HEATER STACK
57. WATER HEATER
58. RESIDUE-DISPOSAL CONVEYORS
59. LIMEROCK-PRECIPITATE SAMPLE TANK
60. COPPER-CADMIUM PURIFICATION TANKS (7)
61. COBALT PURIFICATION TANKS (5)
62. COLD-WATER STORAGE TANK
63. HOT-WATER STORAGE TANK
64. COPPER-CADMIUM PURIFICATION FILTER PRESSES (4)
65. COBALT PURIFICATION FILTER PRESSES (4)
66. FILTER-PRESS PUMP GROUP
67 MIXING TANK FOR BETA-NAPHTHOL AND CAUSTIC SODA SOLUTION
68. LIME-PULPING TANK
69. HYPOSULPHITE OF SODA DISSOLVING TANK
70. GLUE-DISSOLVING TANK
71. SHIFT CHEMISTS' LABORATORY
72. COPPER-CADMIUM PURIFICATION BYPASS TANK
73. COBALT-PURIFICATION BYPASS TANK
74. FILTER-CLOTH WASHER
75. NEUTRAL FILTRATE AND TOWER PUMP GROUP
76. EVAPORATING TOWER
77. EVAPORATING-TOWER BLOWER
78. RESIDUE FILTRATE AND WASH-WATER PUMP GROUP
79. PURE-SOLUTION PUMP GROUP
80. PURE-SOLUTION SUMP
81. CHLORINE-REMOVAL FILTER PRESSES (4)
82. SILVER-REDUCTION PACHUCAS (2)
83. CHLORINE-REMOVAL PURIFIERS (2)
84. RESERVE COBALT PURIFIER
85. 28-FT. DORR THICKENER
86. WATER BALANCE TANK
87. GRANULAR-RESIDUE STORAGE BIN
88. 10" BELT ELEVATORS (3)
89. FINAL ROASTING SLUDGE TANK
90. FINAL LEACH BOXES (3)
91. PRIMARY LEACH BOXES (3)
92. TUBE MILLS (2)
93. DUPLEX DORR CLASSIFIER
94. MILL-WATER BALANCE TANK
95. FORRESTER BOX
96. MINERALS SEPARATION FLOTATION MACHINE (8 BOXES)
97. MILL-WATER TANK

FIG. 6.—GENERAL PLAN OF LEACHING AND PURIFICATION DIVISION.

10. Precipitation of chlorine by silver sulphate followed by filtration and regeneration of silver sulphate. Only 6 to 7 per cent of the solution is so treated.

11. Cooling and concentration of the solution by evaporation, and delivery to the pure solution storage of the electrolytic division. Fig. 5 is a flow sheet of the leaching and purification division and Fig. 6 a general plan.

Details of Operations

1. Leaching is carried on in nine 12-ft. dia. 34-ft. stave Pachucas, having a 20-in. dia. wooden column and a 60° cone bottom. Spent solution is drawn from the storage tanks of the electrolytic division through two 8-in. lead pipe lines controlled by rubber pinchcocks. Calcine is weighed from a storage bin into cable-drawn hopper trucks of 5 tons capacity, which discharge either directly into the Pachucas or into reserve charge bins, of which each Pachuca has two. Agitation is effected by compressed air delivered from the outlet plug cock; the pressure of the air normally used is 30 lb. per sq. in., and during actual charging of calcine 90 lb. per sq. in. The working charge of a Pachuca is 16,000 gal. of spent solution, and from 17,000 to 20,000 lb. wet weight of calcine, the latter varying according to the acidity of the spent solution, and the grade and sulphate content of the calcine, and is altered from time to time to ensure that the acidity of the pulp does not fall below about 5 grams per liter in the first stage of leaching. The spent solution normally contains 50 to 55 grams per liter of zinc and 90 of sulphuric acid, but as the calcine does not always contain sufficient zinc sulphate to replenish sulphate losses from solution, the spent solution is frequently fortified by addition of sulphuric acid delivered by the acid plant to the storage tanks. The initial acidity of each Pachuca charge of spent solution is determined before addition of the calcine. After the calcine is charged leaching is continued for 1½ hr.; the acidity of the pulp is determined and a further addition of calcine, usually 500 to 1500 lb., is made, as calculated to reduce the acidity to 1.5 grams per liter. Agitation is continued a further ¾ hr., the final acidity is checked and the pulp is discharged. Spent solution has a temperature of about 30° C. and the pulp in the Pachucas rises to 50 to 55° C. Filling and discharging require 20 to 30 min., and the cycle is thus of about 3¼ hr. duration. Circuit flow is about 750,000 gal., and calcine leached 400 tons dry weight daily.

2. The Pachuca pulp is discharged into a brick-lined launder leading to six duplex Dorr classifiers arranged in parallel. The classifiers are about 16 ft. long, with a slope of 1 in 6; each ladder has 39 bronze rakes 22 in. long and makes 10 strokes per minute; the backboard is

24 in. high and classification is at from 100 to 150 mesh. Owing to the variations in rate of flow from the discharging Pachucas, the classifiers are working under a difficult condition; nevertheless, the granular residue separated contains about 75 per cent of the sulphides in the pulp, and 90 per cent of the unleached zinc oxide. The granular residue is conveyed to the flotation plant by 12-in. push conveyors, working in horizontal wooden troughs. The push blades are of stainless-steel sheet suspended on bronze hangers. The classifier overflow is joined by the tailings from the flotation plant and passes to Dorr thickeners.

3. The principal equipment of the flotation plant used for the treatment of the granular residue comprises two tube mills (5 ft. dia. by 10 ft. and 16 ft. long, respectively), small duplex Dorr classifier, bucket elevators, eight Minerals Separation subaeration flotation boxes (3 ft. sq. by 4 ft.), one Forrester flotation box (10 by 4 by 4 ft.) and two sets of three-compartment continuous leaching boxes, one set agitated mechanically and the other by air. The treatment is carried out in a zinc sulphate solution, the neutral solution used for pulp dilution, etc., being supplied from the by-pass liquors of the purification process.

The granular residue contains approximately 20 to 25 per cent of zinc oxide and 40 to 45 per cent zinc sulphide. It is ground in one of the tube mills, diluted with neutral solution, partly leached with a limited amount of spent solution, in the mechanically agitated leach box, and then classified at 150 to 200 mesh. Classifier oversize returns to the tube mill and the overflow passes to the flotation boxes. It is a necessary condition to successful flotation that sufficient zinc oxide remain in the pulp to restore neutrality and precipitate all iron present. To ensure rapid precipitation of the iron, manganese dioxide cell sludge in small quantity is ground with the granular residue. As a promoter of flotation, a crude copper sulphate, made by mixing copper residue from the cadmium plant with sulphuric acid, is also added to the tube-mill feed. The frothing agent used is eucalyptus oil, which is added to the first and third M. S. boxes and to the Forrester box. A concentrate is taken from the first 6 or 8 M. S. boxes, and a middling from the remainder. The Forrester box is used to clean the spigot product from the M. S. box, the froth product joining the M. S. middlings and returning to the first M. S. box. The tailings are leached with a small excess of spent solution, and flow back to the main plant to join the classifier overflow. The concentrate is flushed to a Dorr thickener, from which thick pulp is drawn to a small Moore filter unit. The filtered concentrate is weighed out to the preroast division. About 35 to 40 tons of granular residue is treated daily for the production of up to 20 tons of concentrate, assaying 45 to 50 per cent zinc and 20 to 23 per cent sulphide sulphur (roughly up to 60 to 70 per cent zinc sulphide), with a sulphide recovery of 95 per cent. The consumption of flint pebbles is 7 to 8 lb. per ton ground, of manganese dioxide sludge 90 lb. per ton, of copper 3 to 4 lb. per ton and of eucalyptus about 1.7 lb. per ton.

Sludge from the ventilating system of the final roasting division and lead sulphate sludge from the preroast and acid divisions are added to the flotation tailings in the final leaching unit.

4. Classifier overflow and flotation tailings pulp unite and flow into five Dorr thickeners in parallel; various by-pass and spillage liquors, solution returned from the cadmium division, cobalt precipitate sludge, etc., are also fed to these thickeners. The thickeners, 50 ft. in diameter, are built of 15-ft. staves, lead-lined, with a bottom of bitumen-jointed concrete. Four aluminum-bronze plow arms are supported at 16° to the horizontal by copper tie rods and a central lead-covered 4-in. steel shaft, making 7½ revolutions per hour. Peripheral launders collect the overflow.

The feed pulp contains about 30 grams per liter solids, or 1 to 44 solids to solution by weight; the overflow solution contains about 1 gram per liter of solids, including, in addition to residue slimes, cobalt precipitate and uncoagulated silver chloride resulting from the reaction of silver sulphate in the calcine with chloride in the spent solution, neither of which solid settles well. The overflow gravitates in launders to the limerock precipitation tanks. The underflow, thickened to a 1:3 pulp, is raised by air lifts to thickening tanks, where it is settled and thin pulp is decanted back to the Dorr thickeners, leaving a 1:1½ pulp (sp. gr. 2.0). This latter is air-agitated with limerock pulp, which neutralizes the solution, precipitates iron, silica, etc. and brings the pulp to a free filtering condition, ready for the next operation. The air lifts used have a submergence of 27 ft. and a net lift of 12 ft. The rising pipes are rubber hose; the foot piece and jet are bronze. The thickening tanks are fitted with hoses for decanting and with a Pachuca column, terminating halfway up the tank.

5. The prepared residue pulp is filtered in a Moore vacuum filter unit. The filter consists of 22 leaves of 80 sq. ft. filtering area, at 6-in. centers, and a cake about 1½ in. thick is formed in 10 to 20 min. The cake is washed with 1.6 to 2.0 times its final water content (which takes 40 to 50 min.) and after a partial drying under vacuum for 15 min. the cake is discharged into hoppers. Each cake weighs approximately 11 tons on discharge and contains 6 tons dry residue, which contains from 0.3 to 0.5 per cent water-soluble zinc and 0.2 to 0.3 per cent acid-soluble zinc. The output is approximately 106 tons per day. The filtrate passes to a receiver connected to vacuum pumps by a barometric leg and moisture trap, and is pumped thence to join overflow from the Dorr thickener. The wash filtrate or the weaker portion of it may be diverted to a wash-filtrate receiver, and thence to the strong wash system subsequently described.

A 25-ton electric crane is used for the movement of filter baskets. The filter cake is fed from the hoppers by screw feeders into three rotary driers, heated directly from coal fires. The drums are 44 ft. long and respectively 4 ft. 3 in., 5 ft. 8 in. and 6 ft. 6 in. in diameter. The moisture content is reduced from 40 to 43 per cent to 18 to 20 per cent, with the evaporation of 50 tons water per day and a coal consumption of 11½ tons. The fireboxes are under forced draft and burn 17 lb. of Tasmanian coal per hour per square foot of grate area. The waste gases have a temperature of 200° to 300° C., and are exhausted by the natural draft of a stack. The dried residue discharges onto a heat-resisting rubber-belt conveyor, passing under the ends of the drums. A second conveyor delivers the residue to a bin, whence it is trucked to the wharf for shipment to the lead smelter at Port Pirie, for realization.

Typical assays of the residue are: Zn, 21.9 per cent; Pb, 6.4; Fe, 31.1; Ag, 5.5 oz. per ton; Au, 0.02 oz. per ton; sulphate S, 2.33 per cent; sulphide S, 1.5 per cent.

6(*a*). Limerock pulp for neutralization of the solution is prepared from lump rock obtained from quarries at Ida Bay, southern Tasmania. The rock is reduced to ½ in. by a jaw crusher, 16 by 9½ in., working at 200 strokes per minute, and high-speed Cornish rolls, 14-in. face and 90 to 98 r.p.m. The latter are in closed circuit with a ½-in. mesh trommel fed by bucket elevator. The crushed rock is ground with flint pebbles in two tube mills, in series and in closed circuit with a simplex Dorr classifier. The mills are 4 and 5-ft. dia., respectively, by 10 ft. long and make 30 r.p.m. The classifier is 24 in. wide, 14 ft. long with a slope of 3 in. per foot and 27-in. backboard; it makes 14 strokes per minute. It is assisted by a cone classifier 4-ft. dia. rim, 4 ft. 3 in. deep, ¾-in. spigot. A small amount of mill water is fed to the No. 1 mill and cone-classifier underflow is distributed between No. 2 mill feed and the Dorr classifier. A large flow of mill water joins the pulp running from No. 2 mill to the classifier. The cone-classifier overflow is settled to a thick pulp in 12-ft. dia. 8000-gal. tanks, overflow returning to the mill circuit. The settling tanks are decanted periodically, and the pulp is discharged to a skip in which it is hoisted to two 16,000-gal. storage Pachucas, each capable of holding 6 to 7 days supply of pulp.

A fan draws dust-laden air from the rolls and elevator casings and delivers it to a scrubbing tower through which mill water is circulated.

About 88 tons of limerock is crushed weekly; the crushing rate is about 2.0 tons per hour, and the grinding rate 1.6 tons per hour, flint-pebble consumption being 3 lb. per ton. The limerock contains 51 to 52 per cent CaO, the pulp contains 58 to 60 per cent solids and the screen analysis is: +150 mesh, 4 per cent; +200 mesh, 10 per cent; −200 mesh, 86 per cent.

6(*b*). The solution overflowing from the Dorr thickeners is neutralized with limerock pulp in a series of four agitation tanks of 28-ft. dia., 12-ft. stave. Each tank is agitated by two 9-ft. wooden impellers at 16 r.p.m., and by 30-lb. compressed air delivered through four copper tubes submerged 8 ft. Each tank is connected to the next of the series by four 8-in. rubber hoses 6 ft. from the bottom. The working capacity of the tanks is 32,000 gal. each, but under series flow the contents decrease slightly from tank to tank.

A definite charge of limerock pulp, varying with the solution acidity, is added at intervals to the first tank of the series. The solution in No. 3 tank is tested at regular intervals to check the removal of iron, and, if incomplete, the requisite additional limerock is added. The average time of passage through the series is 3½ hr., but the treatment should be complete in the third tank because the fourth is used as a storage for the filtration section following.

The solution before treatment contains typically 1.5 grams per liter acid, 0.27 iron, and 0.8 to 1.5 silica, with arsenic and antimony in small amounts (As, 0.020 to 0.040 grams per liter; Sb, 0.001). Silica is reduced to 0.1 grams per liter or less, iron to 0.001, arsenic to 0.0001 to 0.0005 and antimony to 0.0001. The reaction is carried on at a temperature of 41° to 43° C. and the limerock consumption amounts to 70 lb. per ton of calcine leached, or 138 lb. per ton of zinc recovered in solution. The limerock charge amounts to considerably more than the theoretical requirement for precipitation of iron and neutralization of acid, owing to the need for the presence of some excess, and to the formation of a considerable quantity of basic zinc sulphate.

7. The limerock precipitate is separated from the neutral solution by vacuum filtration. The precipitate consists essentially of calcium sulphate, ferric hydrate, silica, basic zinc sulphate, and the very fine particles of slime residue carried over from the thickeners, the latter containing some silver chloride; the whole amounts to 7 to 8 grams per liter. The thinness of this pulp, the gelatinous character of some of the ingredients, the large volume to be filtered, and the gains that can be effected by chemical treatment of the precipitate, render the common procedure of cake formation, washing and discharge unsatisfactory. Therefore a primary unit is used for the production of a large volume of clear filtrate, and of a thick pulp, which is subjected to further treatment in secondary and final units (Fig. 7).

The primary unit consists of three concrete filter tanks with sloping bottoms, each holding a filter basket of 44 leaves of 100 sq. ft. filtering area each at 5-in. centers. The inlet and outlet ports of the tanks are operated by rubber plug valves, and are designed to permit very rapid filling and discharge of the tanks. Filtration is carried on for 2 to 3 hr., the filtrate passing to a receiver, whence it is pumped to the copper-

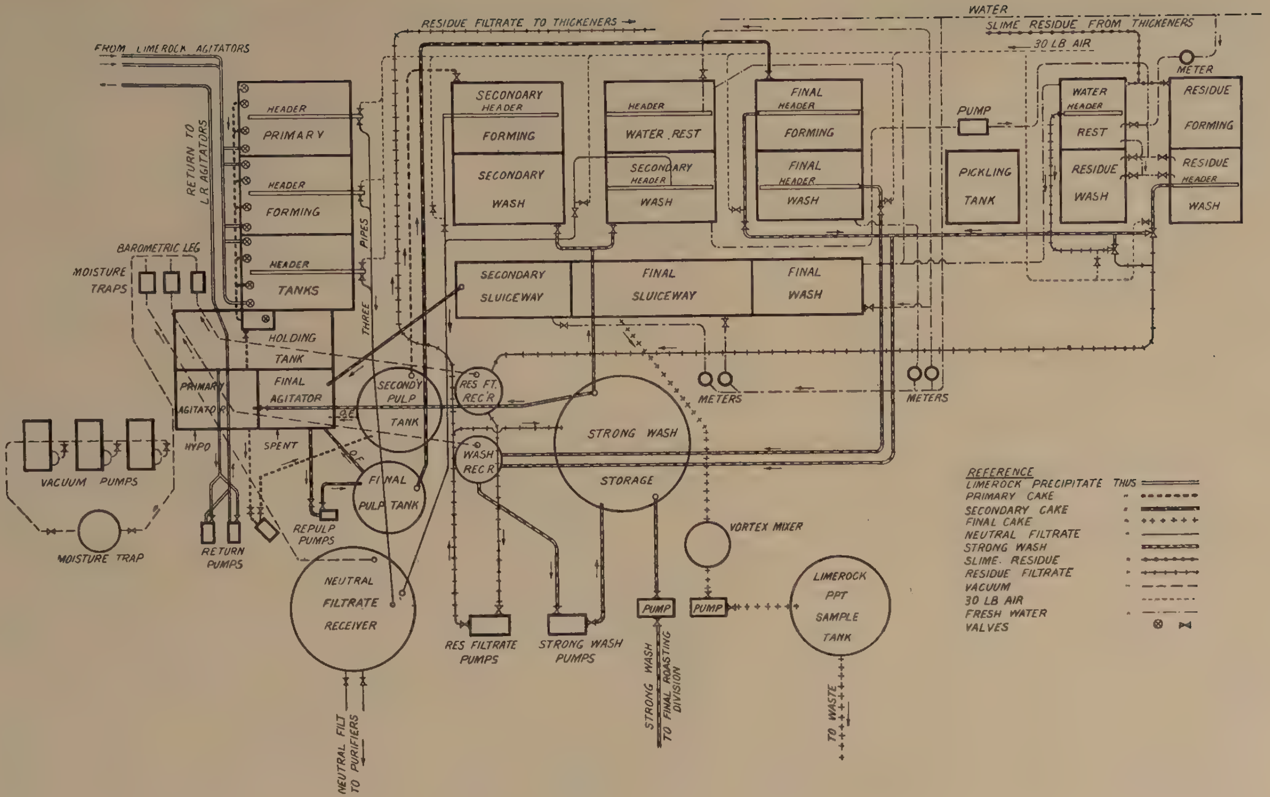


FIG. 7.—DIAGRAMMATIC SKETCH OF FILTER SECTION.

cadmium purification section. At the end of the cake-forming period, the cake being about ¾ in. thick, unfiltered pulp is discharged and pumped back to storage, the cake is discharged to the secondary-unit agitator, the tank is refilled and filtration started again, the complete discharge cycle having taken 15 min. The filter rate varies between 0.05 and 0.07 gal. per square foot per minute, and from 18 to 30 primary cakes are made daily. The temperature of the pulp during filtration is 40° to 42° C.

The secondary and final units each consist of an agitator tank, pulp storage, forming, washing and discharge tanks, and a filter basket of 36 leaves of 90 sq. ft. filter area at 6-in. centers. The agitator tanks are 12 by 9 by 12 ft. deep, each fitted with two impeller shafts rotating in opposite directions; each shaft is fitted with a 5-ft. by 15-in. wooden impeller at the bottom, and two 5-ft. by 8-in. impellers, respectively 4 ft. and 8 ft. higher up.

Pulp discharged from the primary unit is agitated with a controlled amount of strong wash solution (30 to 50 grams per liter zinc) until a smooth pulp is obtained; control of pulp density is maintained by measurement of relative viscosity. A small amount of hypo (sodium thiosulphate) solution is added to extract the silver present. The prepared pulp (temperature about 34° C.) is then filtered, washed with strong wash solution and discharged. The forming time is 30 to 45 min., cake thickness, 1½ in.; washing time, 2 to 2½ hr. and wash volume 1.0 to 1.2 displacements; that is, 1.0 to 1.2 times the volume of liquid in the cake. The filtrate joins that from the primary unit. The hypo consumption is 6.5 lb. per ton of precipitate, or about 2.9 lb. per ounce of silver recovered, the recovery being 70 to 75 per cent.

The discharged secondary cake is sluiced with a limited amount of water to the final agitator, where spent acid solution is added to leach most, but not all, of the basic zinc sulphate present. Hydrogen-ion concentration is determined to guard against the delivery to the filter of an acid pulp; should too much acid be added, the pulp does not filter properly and impurities may be brought back into solution. A small addition of limerock will correct the effect of too much acid. Pulp density is controlled as for the secondary unit. The prepared pulp (temperature about 22° C.) is filtered, washed with 1.1 to 1.25 displacements of water and discharged. Cake thickness and times are as for the secondary unit. The filtrate passes to a receiver, whence it is pumped to the strong-wash storage tank, which supplies the solution for repulping the primary cake and washing the secondary cake, as well as for other purposes connected with control of circuit concentration.

From five to six cakes are made daily in the secondary and final units, each containing about 4.8 tons of precipitate and from 10 to 11 tons of water. The discharged final cake is sluiced with water to a vortex mixer, which produces a smooth pulp; this is pumped to a 14,000-gal. agitator tank where it is measured and sampled before being discharged to waste. The discharged secondary cake contains about 8 per cent water-soluble zinc and the final cake about 0.8 per cent. Other typical assays of the final precipitate are: Acid-soluble Zn, 0.8 per cent; total Zn, 4.8; Pb, 1.0; Fe, 6.6; CaO, 22.5; $CaCO_3$, 2.3 to 3.0; Ag, 0.7 oz. per ton. The production amounts to 26 to 27 tons per day.

8. The neutral solution from the limerock precipitate filters is purified of copper, cadmium, silver, etc., by addition of zinc dust. The operation is carried on in seven 14,000-gal. agitation tanks equipped with an 8-ft. by 9-in. by 9-in. wooden impeller making 22 r.p.m. The amount of zinc dust required to precipitate the impurities is determined every 4 hr. by a rapid electrolytic method. Copper is normally 90 to 120 mg. per liter and cadmium 180 to 240 mg. per liter. The zinc-dust charge is normally 70 to 100 per cent greater than the chemical equivalent of these impurities. This excess is necessary not only to complete the reaction in a reasonable time, but because the least aeration of pulp is apt to cause the cadmium precipitate to redissolve; cadmium precipitation is complete in the agitators but a cadmium-free filtrate is never obtained, even with the substantial excess of zinc dust used, and in spite of precautions against the aeration of the solution at pump glands, etc. As a further guard against aeration the tanks are not completely discharged, about 1500 gal. being left in the bottom each time.

The zinc-dust charge is added in two stages, 90 per cent at the beginning of agitation, and the remaining 10 per cent shortly before filtration commences. The agitation period is 1½ hr. and the purification cycle, charging, purifying and filtering, 2½ hr., the average number of charges being 61 per day.

The precipitate is collected in Dehne filter presses, of which two of a battery of four are used simultaneously. The presses are fitted with plates providing 3 by 3 ft. of filter area on each side; the frames are either 3 in. thick, 48 per press, or 2 in. thick, 63 per press. Each plate is covered with woven-wire or chain-wire screens, to prevent the filter cloths from pressing closely against the plate surface and thus reducing the drainage space. The average filter rate is 0.4 gal. per square foot per minute; the pressure used is up to 60 lb. per square inch, obtained from a 6-in. two-stage centrifugal pump. The filtrate, which contains about 0.1 mg. per liter copper, and from 3 to 7 mg. per liter cadmium, is discharged into launders from which it is distributed to the remaining purification processes, or direct to the evaporating system. The precipitate is dried by blowing with compressed air, and is discharged into trucks for delivery to the cadmium division.

9. The neutral solution contains 20 to 25 mg. per liter cobalt, whereas the solution for electrolysis contains only 10 mg. per liter. From 55 to 60

per cent of the total circuit, therefore, is purified down to 2 to 3 mg. per liter, and blended with the remainder to give the required concentration. Complete removal of cobalt is not practiced because the presence of excess precipitating reagent in solution has a detrimental effect on electrolysis.

Solution from copper-cadmium purification is pumped as required to five agitator tanks similar to those already described, where the cobalt is precipitated by nitroso-beta-naphthol formed in the solution from beta-naphthol and sodium nitrite. As the first portion of the impure solution is being charged, the requisite amount of a caustic soda solution of beta-naphthol is added, with the impeller running; with so little solution in the tank the agitation is violent, and the curd of zinc hydrate and beta-naphtholate, which forms, is thoroughly broken up. When the charge of impure solution (13,000 gal.) is complete, a slight excess of sodium nitrite crystals is added, followed by sufficient spent solution to bring the charge to 0.1 to 0.15 grams per liter acid. The liberated nitric oxide reacts with beta-naphthol to produce nitroso-beta-naphthol, which, in turn, unites with cobalt to give a dark red precipitate. Beta-naphthol consumption is about 9.5 parts per part of cobalt precipitated, and the sodium nitrite consumption is half this amount. The precipitation takes from 1 to 1½ hr. Towards the end of this period the solution is examined for excess reagent, and, if found, steps are taken to adjust the defect. When reaction is complete, the acid is neutralized by addition of a pulp of slacked lime (or soda ash) in excess, agitation being continued until the hydrogen-ion concentration, as determined by a Hellige comparator, is reduced to at least pH 5.4. The lime used is an air-classified commercial product of which nearly the whole is minus 200 mesh. About 35 to 36 charges are made per day, the average precipitation of cobalt being about 94 lb. per day.

The neutralized pulp is filtered in presses similar to those described above, except that most of the frames are only 1½ in. thick, giving a filter area of 1260 sq. ft. per press, this difference being necessary because the precipitate filters less freely. Two presses out of four are in continuous use, the average filter rate being about 0.16 gal. per sq. ft. per min. Pressure used is up to 60 lb. per sq. in., and is produced by a two-stage centrifugal pump. The filtrate is discharged to the evaporating system. The cobalt precipitate is repulped in a small agitator with a little impure solution, and is pumped to the Dorr thickeners, where the acid solution dissolves the zinc hydrate contained in it, and most of the cobalt precipitate floats, and so finds its way into the limerock precipitate and thus to waste.

The reagent solutions used are prepared in steel agitation tanks for which a supply of hot water is available. Fresh stocks of solution are prepared about twice a week.

10. Chlorine can be tolerated in the zinc sulphate solution up to about 75 mg. per liter, and as the normal increase is only about 2 to 2½ mg. per liter per day, chloride removal from 6.5 per cent of the circuit serves to keep the whole solution well below the limit. After copper-cadmium purification, solution is charged in 11,000-gal. batches to two agitation tanks similar to those already described. The solution is brought to an acidity of 0.1 to 0.15 grams per liter by the addition of about 30 gal. of spent solution. The chloride content is determined, and sufficient silver sulphate powder added to precipitate all but 5 mg. per liter of the chloride.

Agitation is continued for an hour, at the end of which time the precipitate is well coagulated; a check is made to ensure that there is still chloride in solution, and, therefore, no excess of silver. If necessary, further solution is added to bring about this condition. The precipitate is allowed to settle, and the solution, when clear, is pumped off through one or more of a battery of four center-feed filter presses. These presses have recessed wooden plates and no frames, as very little precipitate is collected in them. Each press has 35 plates of 6 sq. ft. filter area apiece, and the filter rate varies from 0.6 to 0.3 gal. per sq. ft. per min. according to the condition of the cloth and the fullness of the press. Pressure is up to 35 lb. per sq. in. and is supplied by a single-stage centrifugal pump. The filtrate, which is still acid, passes to the evaporating system, where it joins solution from the copper-cadmium purification and is neutralized by the basic zinc sulphate with which the latter solution is saturated. About 26 lb. of chlorine is precipitated daily.

The silver chloride precipitate settled in the agitation tanks, or retained in the filter press, is collected at the conclusion of every six to nine charges in an 800-gal. Pachuca tank, where it is agitated with water acidified with sulphuric acid and zinc dust. This treatment produces zinc chloride and a metallic silver precipitate. The pulp is filtered in open boxes with a false bottom covered with coir matting and filter twill, and connected below this to a wet vacuum pump. The filtrate of zinc chloride is discharged to waste. The silver precipitate is washed and then heated with sulphuric acid in shallow semisteel pans to regenerate silver sulphate. Excess acid is fumed off. The silver sulphate is ground in a small ball mill containing cast steel balls and is then ready for further use. The sulphuric acid fume is drawn off from the hoods of the converting pans by a fan, and is delivered to the Cottrell precipitator of the final roasting division.

The silver sulphate accumulates impurities from the solution, notably calcium sulphate and silica. The former is kept in check by dissolution in the water in which the reduction of chloride is effected, and can be further removed as necessary by agitating the silver precipitate in fresh water, preferably at 40° C. Silica can be removed by leaching silver chloride precipitate in a hypo solution, or by leaching silver sulphate in chloride-free water, followed in both cases by filtration to remove the residue, and precipitation of silver from the solution by means of zinc dust. The silver sulphate stock is normally maintained at 40 to 49 per cent silver—i.e., about 58 to 70 per cent pure—and the recovery of silver in the cycle is 97.5 to 98 per cent.

11. The filtrates from the three purification processes are collected and pumped to the distributing launders of a cooling and evaporating tower. This tower is about 23 ft. square and 53 ft. high. The solution is fed to distributing launders 15 ft. below the top, and flows from them over horizontal 2-in. square hardwood baffles to a concrete sump at the base of the tower. A layer of coke is provided above the inlet channels to prevent loss of spray. Forced draft is provided by a fan that delivers about 100,000 cu. ft. of free air to the tower per minute. The pressure at the base of the tower is ¾ to 1 in. water gauge and below the cake layer ⅝ inch.

The inlet solution has a temperature of 38° to 40° C. and the outlet solution of 20° to 22° C. The air is taken in at atmospheric condition, usually with a relative humidity of about 60 per cent, and is discharged at about 29° C. saturated with water vapor. The evaporation effected amounts to about 24 gal. per 1000 gal. of solution, or 14,000 gal. per day.

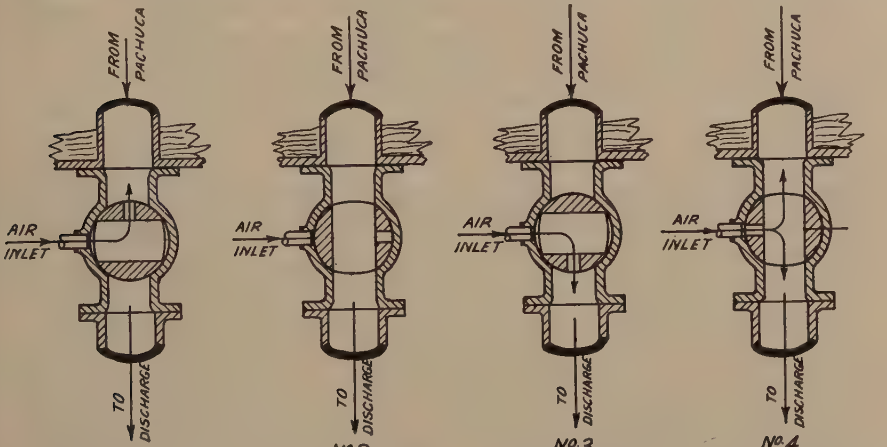
A considerable amount of calcium sulphate and basic zinc sulphate is deposited from the cooling solution on the baffles and tower walls and supports. This deposit reaches an inch or more in thickness in the course of six months. The baffles have to be removed, and the whole interior and baffles have to be cleaned twice a year. From 60 to 100 tons of deposit is removed on each occasion.

The cooled solution discharges from the tower sump into a 45,000-gal. concrete collecting sump, from which it is pumped by two-stage 6-in. centrifugal pumps through one of two 10-in. steel mains to the pure-solution storage tanks of the electrolytic division.

It is important that the zinc content of the solution for electrolysis should be maintained at a steady figure and to this end the circuit volume must be prevented from fluctuating too widely. Water enters the circuit chiefly as wash water at the residue and limerock precipitate filters. Smaller amounts enter with limerock pulp, with reagents for purification and as rain water in exposed storage tanks. Water leaves the circuit by natural evaporation from tank surfaces and by accelerated evaporation in the towers described and as moisture in outgoing residues and products.

To avoid the addition of dilute solutions to the main circuit and to aid in keeping the desired balance, the two stages of treatment described for limerock precipitate have been developed and a secondary "strong-wash" circuit established. The volume of wash water that can be used is considerably increased by using this strong wash solution for purposes that result in its concentration, such as wetting down hot calcine from the roasting plants and for irrigating the towers in which warm air from the ventilating systems is scrubbed.

Most of the leaching division's equipment is of more or less standard character, but there are some local features of interest. The acid solution conveyed from the electrolytic division in 8-in. lead pipes is controlled at the Pachuca tanks by rubber hose closed with pinch cocks. The hose, 5 ft. long by 8¾-in. internal diameter, made of acid-resisting rubber, fits over the 8-in. lead pipe and is clamped to it. Bronze stiffening rings are inserted into the lead pipe to prevent collapse. Where used only occasionally such pinch cocks are satisfactory, but with frequent use, as at the Pachuca inlets, the life of a hose is relatively short, being from 10 to 12 months. To reduce the liability or extent of a burst hose, these are reinforced with wrappings of green hide (raw hide).



Nº 1 NORMAL OPERATING POSITION. AIR AGITATION.

Nº 2 NORMAL DISCHARGING POSITION. AIR OFF.

Nº 3 PACHUCA SEALED. AIR CAN BE USED FOR FREEING DISCHARGE

Nº 4 SPECIAL DISCHARGING POSITION. ASSISTED BY AIR

FIG. 8.—OPERATING POSITIONS OF "CORSTORPHAN" PLUG COCK.

Pachuca tanks subject to severe abrasion and to the action of acid up to 55° C. are built of celery top pine, a rather rare local timber, which has proved to be superior to any other available for this purpose. These tanks have been in continuous use for nearly 15 years without replacement. The air columns subject to the most severe abrasion are hooped with copper covered with ½-in. rubber hose and have a life of 5 to 6 years.

The outlet cock—the "Corstorphan"-type plug cock (Fig. 8)—was developed at Risdon for use on the outlets of Pachuca and other tanks where air agitation is required. With the cock in the open position, a hole is drilled through the walls of both body and plug on one side, and the air supply is connected to the body at this point. Four distinct positions of the plug relative to the body are thus created, which enable air to be admitted or excluded when the cock is both open and shut.

The slightly acid leach liquors containing ferric and copper sulphates are highly corrosive and many types of alloys have been used in apparatus for handling them. One of the most resistant is an aluminum-silicon bronze containing 90 per cent Cu, 9 per cent Al and 1 per cent Si, but difficulty in getting uniformly sound castings limits its use.

The metal saucer forming the apex of the cone in the Pachuca tank is a bronze of 90 per cent Cu, 10 per cent Sn, as is the outlet plug cock attached to it. Below the plug cock is an aluminum-silicon bronze bend leading into a short length of wood-stave pipe which delivers into the wooden launder that in turn discharges into the classifiers. Classifier rakes are of aluminum-silicon bronze. Push-conveyor blades are of Staybrite steel sheet carried by aluminum-silicon bronze hangers. Dorr-thickener steel shafts are lead-covered below the solution. This lead is to be replaced with rubber hose, as necessary. Originally thickener arms were of lead-covered mild steel. Failure of the lead allowed corrosion of the steel. Arms of 87.0 per cent Cu, 10 per cent Al, 3.0 per cent Fe also failed, but bronze of 90 per cent Cu, 10 per cent Sn has given good satisfaction and is now standard. Bronze spiders to which the arms are attached have been in service 15 years. Stays are 1-in. copper rods.

The arms are cast in sections with spigot and socket joints secured by cotter bolt. The rakes are integral with the arm, but as they wear are being replaced by detachable rakes of aluminum-silicon bronze (90 per cent Cu, 9 per cent Al, 1 per cent Si) which is equally resistant to corrosion and more resistant to abrasion.

Lead pipes are generally used where solutions are acid. After neutralization with limerock, solutions deposit gypsum and basic zinc sulphate, which necessitates frequent cleaning of pipe lines. To facilitate this, copper pipe, which is lighter to handle and not so easily distorted, has largely replaced lead. After purification cast iron or mild steel is used.

The framework of the leaves in the vacuum filters is composed of three 1¼-in. by 8-gauge (I.S. W.G.) copper-tube members, assembled with bronze fittings and supported on a wooden head beam by bronze bolts. Two members each form one side and half the bottom, and are connected by a T-piece to a central outlet member. The bolts and outlet pipe which pass through the head beam are carefully packed with rubber insertion to guard against leakage of pulp into the head of the leaf when it is submerged. Riveted to the head beam are T-bolts, which support the leaf in the filter-basket frame by means of cotters; the bases of T-bolts and rivets are covered with rubber to prevent possible metallic connection between the leaf framework and the basket frame, a condition that may result in electrolytic corrosion. The bottom members of the frame are slotted or drilled to permit entry of filtrate, which is drawn off through the central outlet pipe. The latter has a special coupling at the

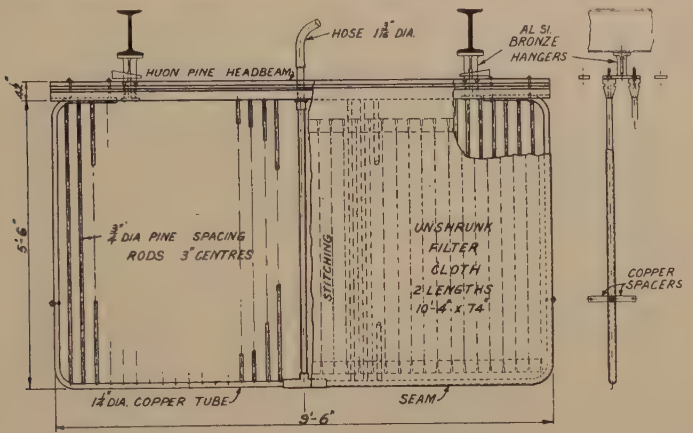
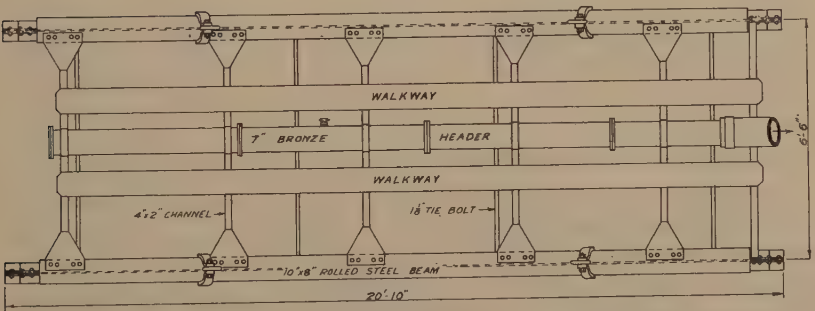
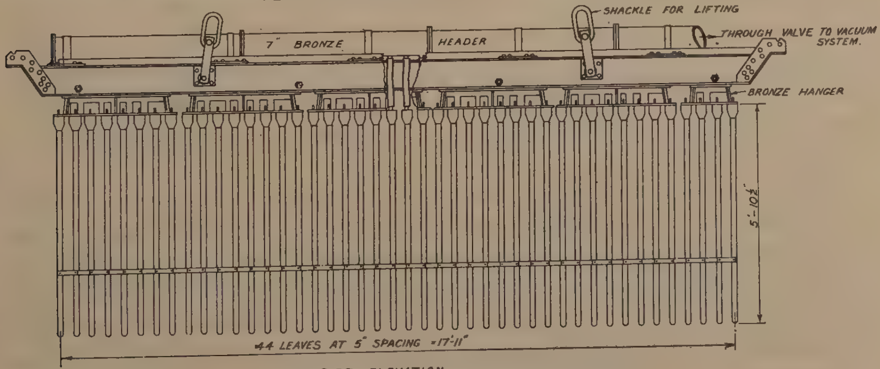


FIG. 9.—VACUUM FILTER LEAF.



PLAN - LEAVES OMITTED


SHACKLE FOR LIFTING
7" BRONZE
HEADER
THROUGH VALVE TO VACUUM SYSTEM.
BRONZE HANGER
5'-10½"
44 LEAVES AT 5" SPACING =17'-11"

SIDE ELEVATION

FIG. 10.—VACUUM FILTER BASKET.

head beam to facilitate replacement of the leaf cover; it is connected to the basket filtrate manifold by rubber hose. Each frame has a cover of cotton filter cloth prepared with sewing machines. The two sides are joined by vertical lines of stitching 3½ in. apart, forming pockets into which ¾-in. wooden rods are inserted to provide drainage space within the leaf. To fix the cover to the frame, the center pipe is uncoupled at the head beam and the cover is slipped over it. The cloth is then joined round the side and bottom members by hand stitching and after the wooden rods are inserted the top edges are cleated to the wooden head beam. The life of the copper-tube frames is upwards of five years. Staybrite steel-tube frames in use since 1929 show little or no deterioration and are definitely superior to copper tube in this service. Details of the leaf frame and the assembly of the filter basket are illustrated in Figs. 9 and 10.

The service rendered by filter cloth is a matter of importance. At all stages following the limerock precipitation, and up to the leaching Pachucas in the next replenishing cycle, the solution is saturated with calcium sulphate, which tends to crystallize out with decrease of temperature or increase of sulphate-ion concentration, and hence with increase of hydrogen-ion concentration. Deposition of calcium sulphate in the pores of filter cloth is general in all the filtering operations, but particularly so in the limerock-precipitate primary filters. The latter are also subject to the deposition of basic zinc and copper sulphate, which clogs the filters badly but which is readily removed by pickling in a dilute acid solution.

The removal of the calcium sulphate is more difficult; simple washing and a vibratory process are both employed on occasion. The limerock-precipitate primary filters are placed in a tank of water for periods of two days in every five, during which all the water to be used in washing slime residue and limerock precipitate is first passed through the filter leaves in the reverse direction to the flow when filtering, or, when the water contains appreciable sediment, it is merely passed through the tank containing the filter. The filter leaves in the limerock secondary and final units may be stripped of their covers, which are then washed in warm water (calcium sulphate has maximum solubility at about 40° C.) and replaced on the frames.

The vibratory method of cleaning is operated as follows: A fouled filter leaf is laid on a table and filled with water. The water supply must be sufficient to keep the leaf full in spite of what filters through the cloth during the cleansing process. The whole surface is then rubbed over with a blunt-edged tool held in an ordinary pneumatic hammer. The calcium sulphate is very rapidly loosened by this treatment, and the flow of water at once removes it. Filter-press cloths are reconditioned by tumbling in successive washes of warm water in a closed wooden drum containing baffles.

Metallurgical and operating details of the leaching division are shown in Table 2.

TABLE 2.—*Metallurgical and Operating Data of Leaching Division*

AVERAGES FOR FOUR-WEEKLY PERIODS FOR YEAR 1934–35 AND UP TO APRIL 29, 1936

	Average 1934–35	Average Year 1936 to Apr. 29
Pachuca Section		
Calcines leached, tons		
Preroast	24	904
Final roast	9,278	10,260
Total	9,302	11,164
Assay: Ag, oz	2.2	2.0
Pb, per cent	1.6	1.6
Sol. Zn, per cent	53.2	53.0
Zn, per cent	59.1	59.2
Sol. SiO_2, per cent	1.27	1.15
Tot. S, per cent	2.22	2.63
Sulphate S, per cent	1.30	1.27
Sulphide S, per cent	0.92	1.36
Spent solution: acid, grams per liter	90.1	90.8
Acid added to circuit, tons	257	320
Production factors, per cent calcine leached:		
Granular residue	7.50	8.97
Concentrates	3.43	4.87
Slime residue	27.54	26.60
Limerock precipitate	6.90	6.76
Flotation Section		
Granular residue fed, tons	697	1,001
Assay: sulphide S, per cent	9.70	12.42
Concentrates produced, tons	319	544
Assay: Ag, oz. per ton	11.4	8.75
Pb, per cent	1.5	1.5
Zn, per cent	48.2	48.5
Total S, per cent	22.84	24.26
Sulphate S, per cent	2.51	2.28
Sulphide S, per cent	20.33	21.98
Tailings assay:		
Acid-sol. Zn, per cent	1.23	0.65
Sulphide S, per cent	1.50	1.54
Eucalyptus used, lb	1,350	1,743
Lb. per ton granulated residue	1.94	1.74
Residue Filtering Section		
Slime residue produced, tons	2,561	2,970
Assay: Ag, oz	6.2	5.6
Pb, per cent	6.0	6.1
Water-sol. Zn, per cent	0.43	0.43
Acid-sol. Zn, per cent	0.22	0.28
Total Zn, per cent	21.7	21.7

	Average 1934–35	Average Year 1936 to Apr. 29
Residue Filtering Section (*Continued*)		
Total S, per cent	3.32	3.98
Sulphate S, per cent	2.25	2.01
Sulphide S, per cent	1.07	1.97
Residue Drying Section		
Moisture: Feed, per cent	43.13	41.77
Discharge, per cent	19.37	19.86
Evaporated, tons	1,320	1,394
Coal consumed, tons	289	319
Moisture in coal, per cent	4.57	4.37
Limerock Agitation Section		
Limerock used: tons	314	351
Lb. per ton calcines	76	70.5
Assay: Fe, per cent	0.25	0.25
CaO, per cent	50.9	51.5
Solution entering agitators, grams per liter:		
H_2SO_4	1.51	1.56
Fe	0.21	0.26
SiO_2	1.41	1.31
Solution after limerock, mg. per liter:		
Fe	1.02	1.3
As	0.11	0.1
Limerock Precipitate Filtering		
Limerock precipitate, tons	642	754
Assay: Ag, oz. per ton	0.83	0.93
Pb, per cent	0.84	0.85
Water-sol. Zn, per cent	0.97	0.81
Acid-sol. Zn, per cent	0.62	0.85
Total Zn, per cent	4.9	4.86
Unconsumed $CaCO_3$, per cent	4.15	2.6
Hypo used, lb	3,342	4,961
Lb. per ton precipitate	5.2	6.6
Purification Section		
Impure solution:		
Copper, mg. per liter	94	95
Cadmium, mg. per liter	208	191
Zinc dust used: tons	35	50
Lb. per ton cathode Zn	16.60	19.56
Zinc-dust precipitate, tons	114	144
Assay: Ag, oz. per ton	13.55	11.54
Pb, per cent	1.15	1.20
Zn, per cent	32.6	33.4
Cu, per cent	7.35	7.4
Cd, per cent	12.60	11.6
Content in lb. per ton cathode zinc:		
Zn	17.6	19.0
Cu	4.0	4.2
Cd	6.8	6.5

TABLE 2.—(*Continued*)

	Average 1934–35	Average Year 1936 to Apr. 29		Average 1934–35	Average Year 1936 to Apr. 29
Purification Section (*Continued*)			Purification Section (*Continued*)		
Cobalt removed, lb.	2,028	2,636	Pure solution assays:		
Beta-naphthol used: lb.	19,796	25,294	Zn, grams per liter	113.2	111.6
Lb. per lb. cobalt	9.76	9.60	Manganese, grams per liter	6.3	7.9
Sodium nitrite used, lb.	11,571	14,824	Silica, grams per liter	0.099	0.101
Caustic soda used, lb.	6,357	7,926	Cobalt, mg. per liter	10.0	9.9
Lime used, lb.	21,734	34,103	Copper, mg. per liter	0.08	0.08
Soda ash used, lb.	8,741		Cadmium, mg. per liter	6.67	6.1
Chlorine removed, lb.	376	708	Chlorine, mg. per liter	60.4	60.9
Silver loss: oz.	280	525	Antimony, mg. per liter	0.09	0.08
Oz. per lb. chlorine	0.75	0.74	Arsenic, mg. per liter	<0.1	<0.1
			Iron, mg. per liter	1.17	1.1

Filtering Data

Residue filters:

Specific gravity of pulp	2.0
Cake-forming time, min.	10–15
Washing time, min.	35–50
Water used per cake	1½ to 2 displacements, equal to 1600 to 2300 gal.
Loading per cake, lb. dry solids per sq. ft. filter	7½–8
Life of filter cloth	1500 cakes = 3½ months
Filter-cloth consumption, sq. yd. per ton cathode zinc	0.0132

Limerock Precipitate Filters

	PRIMARY FILTER	SECONDARY FILTER	FINAL FILTER
Filter rate, gal. per sq. ft. per min.	0.05–0.07	0.05–0.07	0.05–0.07
Forming time	2 hr.	45 min.	30 min.
Washing time	None	2½ hr.	2½ hr.
Loading, lb. dry solids per sq. ft.			3.3
Ratios of cakes formed	4.71	1.05	1.0
Strong wash solution used per cake, gal.		2,600	
Wash water used per cake, gal.			3,200
Hypo used, lb. per ton precipitate	6.5		
Hypo used, lb. per oz. silver recovered	2.9		
Silver recovery, per cent amount originally in precipitate	71		
Cloth life	1,200–1,400 cakes.		
Filter-cloth consumption, sq. yd. per ton of cathode zinc	0.083		

Purification

Filter-cloth consumption on filter presses, sq. yd. per ton cathode zinc	0.0188

ELECTROLYSIS

Power is purchased from the State Hydro-Electric Commission. It is generated in the central highlands of the island and transmitted at 88,000 volts to the Commission's transformer station adjacent to the works. It is transmitted from this station by underground cables at 11,000 volts three-phase 50 cycles a.c. to the company's station, where it is stepped down to 440 volts for delivery to the rotary converters and for distribution about the works. About 4000 hp. is used at 11,000 volts by synchronous motors driving generators supplying direct current to one small cell room. The maximum demand is approximately 45,200 hp. and the mean load 44,200 hp., of which 39,900 hp. is used for electrolysis and 4300 hp. for plant motors, lighting and heating.

The electrolytic division consists of five cell-room units with necessary feed and spent-solution storage tanks and cooling-water system. Three of these units are housed in one room 482 ft. long by 124 ft. wide; the fourth, of similar size, in a room immediately adjoining, while the fifth is some distance away. This fifth unit, known locally as the "10-ton unit," was the cell room of the first commercial experimental plant at Risdon and now produces 18 to 19 tons of cathode zinc per day. It is served by motor-generator sets with a current of 10,000 amp. at 250 volts. The other four units are each served by two rotary converter sets in parallel with a current of 12,000 amp. at 510 to 520 volts.

Each of these units consists of 144 cells arranged in 24 cascades of 6 cells each. Cascades are arranged in pairs with a 5-ft. walkway between pairs. There is a drop of 5 in. between the cells of a cascade. The over-all length of each cascade is 86 ft., with a space between the upper end and the wall of the building of 11 ft. Between the lower end of the cascade and the wall of the building is a floor space 27 ft. wide, on which are the stripping racks and trucking lines for conveying zinc cathodes to the melting plant. Above the center line of each cascade is a mild-steel beam carrying a crawl and one-ton chain block for lifting and conveying cathodes to and from the stripping floor. All cells of each unit are electrically in series.

Each cell consists of a lead-lined wooden tank, the walls of which are built up of 4 by 1-in. creosoted planks laid on the flat and nailed and doweled together, alternate side and end planks running right to the corner. The cell rests upon a bottom of planks supported by two heavy wooden bearers and the porcelain insulators supporting the latter stand on concrete pillars. Overflow spouts are 6 in. wide. Interior cell dimensions are 154½ by 33½ by 54½ in. and the capacity is approximately 160 cu. ft. In three units the bus bars are carried on the walkway side of each cell, being supported on porcelain insulators on the cell wall. These consist of cast copper 7.5 by 2.5 in., tapering along the length of the cell as the current carried diminishes or increases, as the case may be (Fig. 11). In the fourth unit (of more recent construction) the bus bars are of rolled copper 1¼ in. thick and tapering in width from 16⅜ to 1¾ in. They are supported on edge on porcelain insulators fastened to the side of the cell (Fig. 12). These bus bars are capable of carrying a current of 16,000–18,000 amperes without undue heating.

Each cell has 34 anodes and 33 cathodes, of which the head bars rest on the respective bus bars on one side of the cell and on porcelain insulators on the back of the cell. The anode is a lead plate ⅜ in. thick, 23 in. wide and 3 ft. 7½ in. long cast onto a copper head bar 1¼ by ⅝ in. by 3 ft. 2½ in. long. In the fourth unit this bar is 3 ft. 7½ in. long to meet the altered bus-bar arrangement. The weight of lead in the anode is approximately 160 lb. The spacing between centers of anodes is 4 in. in three units, 3¾ in. in the fourth unit and 3½ in. in the "10-ton unit." The cell voltages corresponding to these spacings are 3.60, 3.56 and 3.54 volts, respectively. The cathode is a rolled aluminum sheet 3/16 in. thick in the submerged portion increasing to ½ in. just below and above the solution line. It is 3 ft. 9 in. long by 2 ft. 1 in. wide and is submerged to a depth of 3 ft. 1¾ in. It is supported between the anodes by two copper bars 1½ by ⅜ in. by 3 ft. 10½ in. long riveted to each side of the top of the sheet, one end resting on the cathode bus bar and the other on porcelain insulators at the back of the cell. Mild-steel lifting lugs are riveted between the copper bars. Each cathode has a small groove

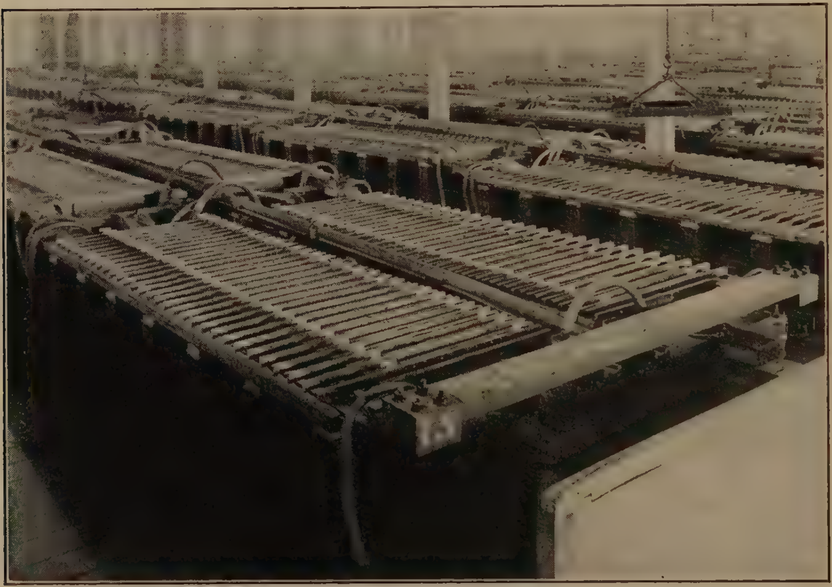


FIG. 11.—ELECTROLYTIC CELL, WITH ELECTRODES.

¼ in. on one side and ⅜ in. on the other side from the vertical edges and is also grooved on the vertical edge. These grooves make a line of weakness in the deposited zinc sheet and facilitate stripping. They have been much more satisfactory at Risdon than wood or rubber-edge strips. The total submerged areas of anodes and cathodes in each cell are 400 sq. ft. and 445 sq. ft., respectively. With a current of 12,000 amp. the anode current density is 30 and the cathode current density 27 amp. per sq. ft., approximately.

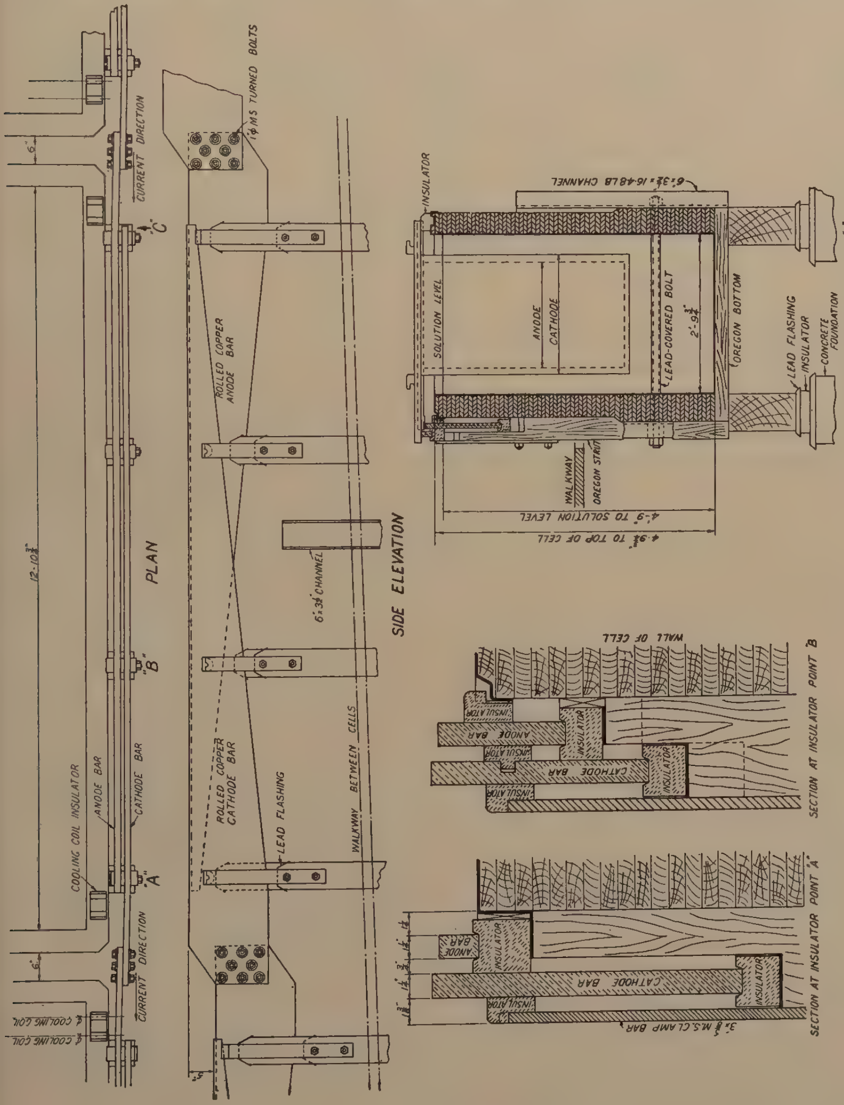


FIG. 12.—ELECTROLYTIC CELL OF FOURTH UNIT, SHOWING BUS BARS.

Provision is made for four cooling coils per cell, although normally only three are required. Two are at each end of the cell and are of 1-in. lead pipe with 31 ft. of submerged length and are supported on porcelain insulating blocks where their ends pass over the bus bars. Two coils are in series; i.e., each coil in a cell is connected to the corresponding coil in the similar cell of the adjoining cascade. Cooling water is supplied from a common 18-in. wood pipe header in the basement through 6-in. risers and diminishing reticulation pipes. The risers are insulated from the header with 2-ft. lengths of rubber hose. The coils discharge into 12 by 10-ft. launders below the floor level, which discharge into a 24-in. wood-stave collecting pipe carrying the water to a pump sump. Fourteen-inch centrifugal pumps force the water through sprays for cooling, after which it is pumped back to the cells through the wooden header previously mentioned. The amount of water circulated varies between 300,000 and 400,000 gal. per hour according to weather conditions. There is a temperature drop of approximately 2.5° C. in the cooling pond and approximately 50,000 gal. per day are required for make-up.

The prepared electrolyte is delivered from the leaching division into six lead-lined storage tanks each 50-ft. dia. and 12 ft. deep. From these it flows through lead pipe lines controlled by rubber pinch cocks to the cells. A 3-in. lead pipe between pairs of cascades has 1-in. connections to each cell of the cascade either side of it and the flow to each cell is controlled by means of a wooden cock. The upper cells overflow into the lower ones and from the last cell the overflow passes into lead-lined launders leading to five 50-ft. dia. lead-lined spent-solution storage tanks.

The new feed to each cell is approximately 1200 gal. per day. At two-hourly intervals there is added to each cell by hand a reagent mixture consisting of glue, beta-naphthol and antimony. The quantity added is 24 mg. of glue, 10 mg. of beta-naphthol and 0.05 mg. of antimony per liter of new electrolyte. The acidity of the cell liquor is determined from time to time by titration of a sample with a standard alkali solution and the feed to the cell so adjusted as to maintain an acidity of 90 grams H_2SO_4 per liter. There is thus removed during electrolysis approximately 60 grams of zinc from each liter (or 0.6 lb. per gallon) leaving a spent electrolyte containing 50 grams zinc and 90 grams sulphuric acid per liter. This is returned to the leaching division for the treatment of new calcine.

The temperature of the electrolyte is maintained as nearly as possible at 35° C. but in very humid weather may rise to 40° C. During electrolysis the cooling coils become coated with deposits of manganese dioxide and gypsum, which interfere with their efficiency and they are periodically removed from the cell and freed from these deposits.

The zinc deposition period is 72 hr. Every third day the cathode sheets with their deposits of zinc are lifted out of the cell in lifts or groups of eleven by means of the overhead chain block, transported to the stripping floor and lowered into the stripping rack, each cathode having a movable arm to itself. The stripper, with a wooden mallet and an angle knife of 3.5 per cent nickel steel, removes the zinc sheets starting from the top, and stacks them lengthwise on end on special trucks. Scrap, which consists of broken sheets and edgings, is loaded onto flat side-tipping trucks. Scrap amounts to from 3.5 to 4 per cent of the total zinc stripped. Loaded trucks are weighed and delivered into the drying tunnel of the melting plant.

The cell is not short-circuited for stripping as only one-third of the cathodes are removed at a time and the remainder are sufficient to carry the full current for this short period. Each cell yields approximately 2150 lb. of zinc each stripping and one man strips 9 cells per day—a total of 8.6 tons per day.

It is essential for satisfactory deposition and stripping of zinc that the surface of the aluminum cathode be kept in a clean and proper condition. A routine of scrubbing 22 cathodes from each cascade stripped ensures that every cathode is scrubbed once in 27 days. In addition, any that through mishap are obviously in need of it are scrubbed, as required. Before scrubbing, the cathode is cleaned by pickling in spent electrolyte for 20 to 30 min. Scrubbing is done with a mechanical, rotary, steel-bristled brush. Prior to scrubbing the cathode surface is rubbed with sandstone, which with the aid of the brush imparts a roughened surface.

The cathode is subject to corrosion and mechanical wear, but it is the former that determines its life. Below the solution line corrosion is practically negligible; above it the zone of maximum corrosion is about 1 in. below the head bar. At the solution line it is considerably less. The life of a cathode ½ in. thick above the solution, as determined by the corrosion at the 1-in. mark, is about four years and at the solution line six years. The full six years of life is obtained in practice by riveting a protecting strip of aluminum on to each side of the cathode above the solution line after approximating three years service, and before the cathode has become seriously weakened. Many paints, varnishes and rubber protection devices have been tried, most of them failures and none so successful as the riveted aluminum strip.

The relative merits of plain and thickened top cathodes depend on the comparative cost, and the value of scrap aluminum. Recently plain 3⁄16-in. sheets are being used. These give a life of three years. The aluminum consumption is 0.4 lb. per ton of cathode zinc produced.

Anodes are not subject to much mechanical wear but they are subject to corrosion, and this is the chief source of the small amount of lead normally present in electrolytic zinc. The amount of lead in the deposited zinc is not, however, necessarily proportional to the rate of corrosion of the anode. With lead anodes it is more a function of anode potential as effected by electrolyte composition and anode current density. Physical destruction by corrosion does not determine the effective life of the anode. This is determined by an age effect on the efficiency of zinc deposition. When new lead anodes are put into use, they require little or no attention for the first six months, other than that of keeping the bus-bar contacts clean. They do, however, become coated with manganese dioxide and lead peroxide scale. At the end of this time they are lifted out singly and cleaned and, if necessary, straightened. The unequal deposition of hard anode scale causes anodes to warp and at 9 to 12 months they are again cleaned and straightened and thereafter at increasingly frequent intervals.

Coincident with this, and particularly after two years, there is a distinct falling off in current efficiency until at three years life this is 1.5 to 2.5 per cent below that obtained with new anodes. That this is not due to more frequent short-circuiting because of warping has been proved by carefully controlled tests. It is evidently due to some change in the anode associated with age. Risdon experience is that three years is the maximum economic life, after which time the lead is cut from its head bar, remelted and cast into a new anode.

About 62 per cent of the original weight of the anode is so recovered and about 21 per cent as a lead dross. The actual wastage of lead in service is 2.6 lb. per ton of cathode zinc produced. The new lead required to cover wastage and dross loss is 6.2 lb. per ton of cathode zinc.

Apart from the influence of the cathode and anode, current efficiency is dependent on electrolyte composition, on the effectiveness of addition agents, on temperature, acidity and period of deposition. With the Risdon electrolyte, containing cobalt, current efficiencies of commercial interest are impossible of attainment without the use of certain addition agents, except possibly at very low acidity and with very short deposition periods, which involve uneconomic use of power and labor. With the use of the addition agents (glue, beta-naphthol and antimony) current efficiencies of 92 to 94 per cent are readily obtained over a 72-hr. deposition period if the electrolyte is maintained at 35° C. and 90 grams per liter acid. Experience has shown that neither glue nor beta-naphthol alone in any amount is as satisfactory as the combination of the two in the proportions used and also that with these two agents the adverse effect of increased acidity and temperature is greatly reduced by the use of antimony. The effect of increases in acidity and temperature when glue and beta-naphthol are used with, and without, antimony is shown in Table 3. Each of these addition agents is toxic if used in excessive amounts. The purified solution normally contains 0.08 mg. of antimony per liter and the addition is designed to increase this to 0.13 mg. This experience does not necessarily hold for electrolytes differing widely from Risdon's, particularly in regard to the cobalt content.

TABLE 3.—*Effect of Acidity and Temperature on Current Efficiency*

Acidity, Grams per Liter	Temperature, Deg. C.	Current Efficiency Loss, Per Cent	
		With 0.05 Mg. per Liter Sb	Without Sb
90	35		
90	40	2.1	3.6
100	35	1.7	6.0
100	40	4.2	7.5

While 72 hr. is the normal stripping period, there have been times in the past when 48-hr. periods were resorted to for short periods in order to maintain good current efficiencies. The current efficiency drop with time is not constant, but is much greater with "bad" than with "good" solutions. With normal conditions the difference in current efficiency between a 48-hr. and 72-hr. deposit is about 0.75 per cent. There has been no departure from the 72-hr. period since the use of the addition agents described. Current efficiencies of closely controlled experimental cells for varying deposition periods are: 12 hr., 95.7 per cent; 24 hr., 95.3; 48 hr., 94.9; 72 hr., 94.0; 96 hr., 93.1.

During electrolysis manganese is oxidized at the anode and precipitated as manganese dioxide. This for a considerable time has just about equaled the amount entering the solutions during leaching, and the manganese content of the electrolyte has remained fairly constant. New anodes are more active in this respect than old ones, but on the average about 0.6 grams of manganese is precipitated from each liter of electrolyte. This, together with gypsum, accumulates in the cell and necessitates cleaning every six to eight weeks. To do this the cell is short-circuited by bolting a copper block across the bus bars and enough of the electrodes are removed from the cell to enable the sludge to be shoveled into a container carried by the chain block. Approximately 5 tons of sludge is removed per day of which the following is a typical analysis: Zn, 4.3 per cent; Mn, 39.8 per cent; Pb, 3.55 per cent.

Apart from the corrosion of anodes and cathodes already discussed, there is no serious corrosion in the cell or building structure. Lead linings of cells are subject to a slight amount of corrosion and to accidental damage, but out of 432 cells in continuous service since 1922 only 125 have had to be relined and in no instance has the timber structure required renewal. Considerable trouble was experienced with some of the first cells built of untreated timber, as borers from the timber perforated the lead lining. Treatment of the timber in hot creosote before construction of the cell completely eliminated this difficulty. Trouble was also experienced with bulging of the side walls of the cell. This was rectified by supporting the walls with vertical channel irons (6 by 3½ in.) held by a heavy lead-covered bolt running through the cell just below the bottom of the electrodes.

TABLE 4.—*Analysis of Pure Solution*

	Grams per Liter		Grams per Liter
Zinc	109.6	Calcium	0.42
Manganese	6.5	Magnesium	3.05
		Sodium	17.35
	Mg. per Liter	Potassium	1.33
		Sulphate (SO_4)	224.1
Cobalt	10.2		Mg. per Liter
Copper	0.14		
Cadmium	4.6	Phosphate (PO_4)	Trace
Silica	101	Aluminum	0.3
Total chlorine	139	Lead	0.08
Chloride chlorine	64	Bismuth	<0.01
Chlorate chlorine	Nil.	Nickel	Not found
Perchlorate chlorine	75	Selenium	Not found
Fluorine	19	Tellurium	Not found
Arsenic	<0.1	Tin	Not found
Antimony	0.11	Silver	0.032
Total nitrogen	327	Solids in suspension	118
Nitrogen as ammonia	321	Specific gravity	1.331

TABLE 5.—*Data on Electrolysis*

Total cathode zinc deposited, 5,674 tons

	Units 1–4	10-ton Unit	Total or Average
Power data			
Average current flow, amp	11,962	9,800	
Average current density, amp. per sq. ft	26.7	26.7	26.7
Average voltage per unit	517	255	
Average d.c. power, hp	33,152	3,349	36,501
Average H.T. a.c. power, hp	35,917	3,930	39,847
Average converting and transmission efficiency, per cent.			
Rotary converters	92.3		
Motor generators		85.2	
Over-all			91.6
Average current efficiency, per cent			92.8
Average cathode zinc deposited per hp-day, d.c. power, lb			12.44
Average cathode zinc deposited per hp-day, H.T. a.c. power:			
In units 1 to 4, lb			11.46
In 10-ton unit, lb			10.80
Over-all, lb			11.39

Glue used, 4,931 lb. = 0.87 lb. per ton cathode zinc
Beta-naphthol used, 2,002 lb. = 0.35 lb. per ton cathode zinc

Table 4 gives a fairly detailed analysis of the pure solution taken in June, 1935.

The data in Table 5 are averages per four-weekly period for 11 periods to April 29, 1936.

MELTING AND CASTING

The melting of cathode zinc with high recovery of clean molten zinc is difficult because of its marked tendency to form dross. This is an inherent characteristic of cathode zinc, and is responsible for the greater part of the dross formed.

Under similar conditions of melting in a coal-fired reverberatory furnace cast zinc can be remelted with the formation of 1 per cent or less of dross while cathodes may give an initial dross formation of from 6 to 17 per cent according to their nature. Their nature in this respect appears to be dependent on the type of electrolyte from which they are produced. For instance, cathodes produced from a cobalt-free solution containing no glue melt with an initial dross formation of about 7 per cent while those produced with the aid of glue from cobalt-bearing solutions, as at Risdon, form about 13 per cent of dross. Cathodes produced from solutions containing 80 mg. of cobalt and 80 mg. of glue per liter, as at Risdon prior to 1929, gave an initial dross formation of up to 17 per cent.

The dross consists of a mixture of zinc oxide and metallic zinc, the metallic portion being in the form of small globules. Each globule apparently is insulated from its neighbor by a film of oxide. By suitable treatment of the dross while hot most of the metallic portion is recovered as molten zinc, while a further portion is recovered by screening the cooled dross. By these means a melting efficiency of about 96 per cent is finally obtained.

The general plan of the melting plant is shown in Fig. 13. There are two hand-fired reverberatory furnaces for melting cathodes, each 21 ft. wide and 39 ft. long, including fireboxes. The crucibles are 16 ft. wide and 18 ft. long. The crucible depth is 48 in. under the charging slots near the firebox end. The capacity when full is approximately 180 tons of molten zinc (Fig. 14).

The furnaces are lined internally with firebrick. The crucible of No. 1 is held in a riveted mild-steel jacket resting on concrete piers and is thus air-cooled underneath. The other one (the first furnace built) was originally constructed on a solid concrete base without a steel jacket, but serious leaking necessitated thickening the walls with concrete and steel-jacketing them on the sides and ends of the crucibles.

The roof of each furnace is flat. It is constructed of specially shaped firebricks held in cast-iron frames supported by the side walls of the furnace and by a heavy steel beam above the center line of the crucible. There are two cast-iron charging holes or slots, one on either side of the center line of the furnace near the firebox end. These openings are 2 ft. 6 in. long and 6 in. wide, their length being at right angles to the center line of the furnace. The tapping spouts are on one side of the crucible near the flue end and the main taphole is 6 in. below the surface of the metal when the crucible is full. A series of lower tapholes is provided for emptying the crucible, if necessary. The tapholes of the two furnaces face each other.

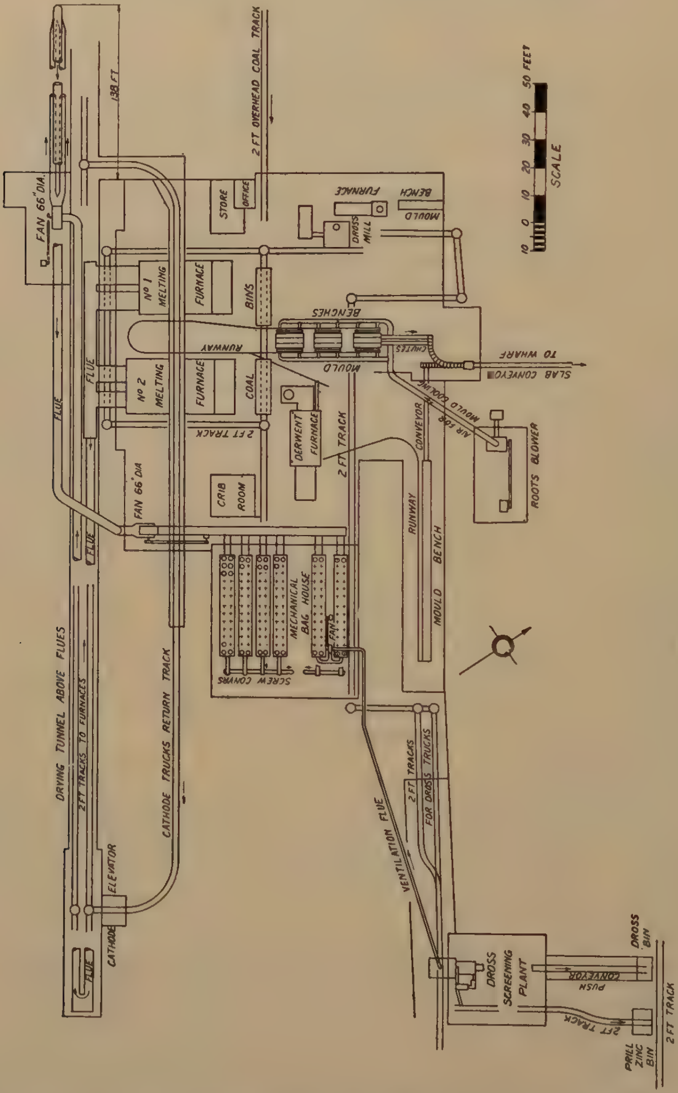


FIG. 13.—GENERAL PLAN OF MELTING PLANT.

In the other, or outer, side wall of the furnace are two drossing doors 3 ft. by 18 in. set just above liquid level. Drossing is done by heavy counterbalanced rakes suspended by crawls from steel beams at right angles to the furnaces. The firebox has a grate area of 146 ft. divided into two sections, and is equipped with forced draft.

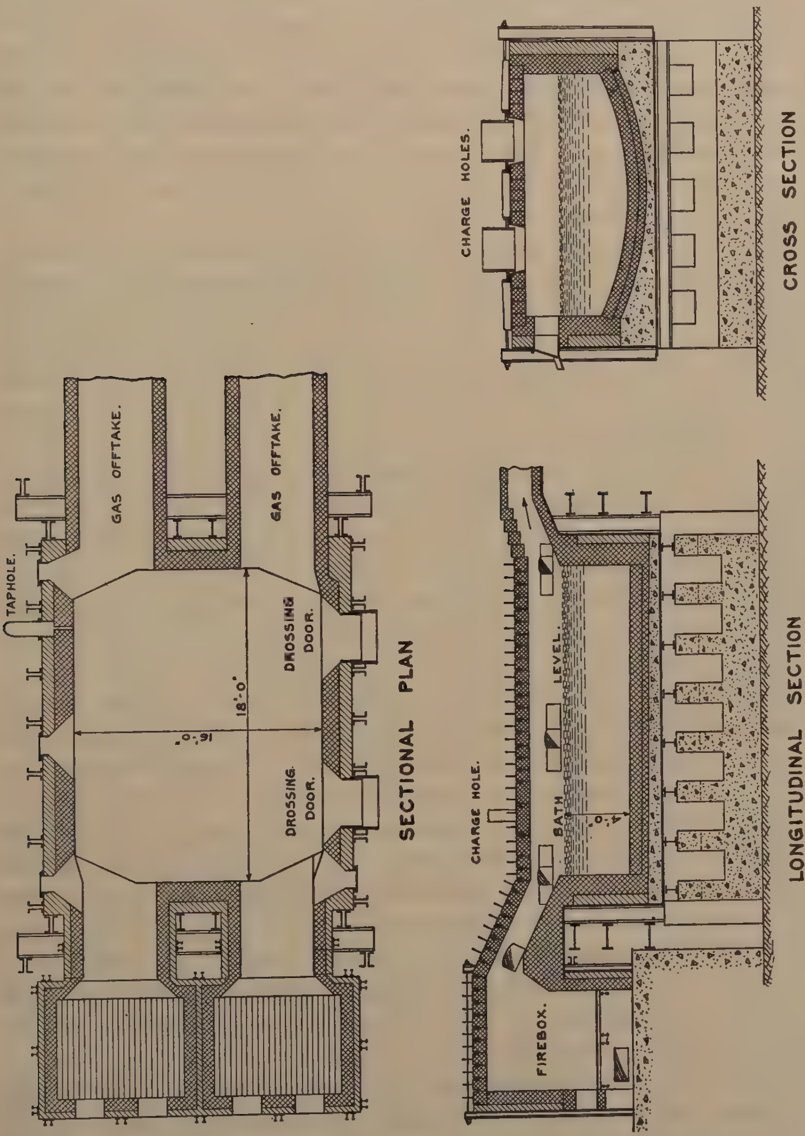


Fig. 14.—Sectional views of melting furnace.

The fire gases enter the crucible through two fire channels inclined downward toward the crucible and leave it by two horizontal flues of rectangular section, which enter a common brick flue along the back of he furnaces. This brick flue is approximately 6 2 ft. long and terminates in a mild-steel flue 1040 ft. long leading to a baghouse. The brick flue and a portion of the mild-steel flue are housed in a building 271 ft. long and varying from 10 ft. 6 in. to 8 ft. 6 in. wide. The walls are of brick and the roof of galvanized iron.

Above the flues are two 2-in. gauge tracks sloping toward the furnaces at an inclination of 1 in 60. These tracks carry trucks loaded with zinc cathodes from the cell room, which are dried by the heat from the flues before reaching the furnaces. About 6 to 8 hr. drying time is allowed. A track from the drying tunnel passes over the charging floor on the top of the furnaces within easy reach of the charge holes. The operating procedure is as follows:

The furnace is fired strongly to heat the metal in the crucible to the desired temperature of about 500° C., any dross from previous operations having first been removed so as to facilitate heat transfer. During this heating period about 12 tons of cathodes, including about 3.5 to 4 per cent of scrap zinc, are withdrawn from the drying tunnel and held convenient to the furnace to be charged. The scrap zinc is tipped onto the charge floor for further drying.

When the furnace is ready to be charged the blast is cut off, the scrap zinc is shoveled in and the cathode sheets are lifted by hand from the truck and dropped vertically on end into the crucible. The depth of metal (48 in.) is sufficient to permit complete submergence of the sheet without undue abrasion of the crucible bottom. The charging operation takes about 30 min. and during this time the temperature of the bath drops to 440° or 450° C.

The fire, which has by now burned low, is raked out and a new fire started and the dross, which is in a mushy state, is warmed up for a few minutes. Ammonium chloride, equal to 1.75 lb. per ton of zinc charged, is now shoveled in through the two drossing doors and immediately stirred into the dross by means of the counterbalanced drossing rakes. Stirring is continued for 10 to 15 min., until the dross becomes red and sandy; then it is drawn out of the crucible into mild-steel side-tipping trucks and taken to the dross mill for further treatment.

While these operations are under way at one furnace, the other is being heated. Each furnace is charged and drossed three times per 8-hr. shift. One shift per week is devoted to chipping dross accretions from the roof and side walls of the crucible.

The dross from the melting furnaces is charged into the dross mill, which is heated and rotated. The zinc liquates out and is tapped. The dry dross is dumped and sent to the dross-screening plant for further treatment. The mill is enclosed in a mild-steel housing with doors for the entry of dross trucks at the mill level. Below the mill are mild-steel hoppers and trucks for receiving the mill discharge, also enclosed in the steel housing. The housing is connected by a flue to a fan that delivers dust and fume to one section of the baghouse. This fan also draws dust and fume from hoods over the drossing doors of each furnace.

The molten zinc recovered at the dross mill runs into a small furnace, from which it is tapped at intervals and cast into standard molds.

The result of the ammonium chloride treatment and of the tumbling in the mill is apparently to destroy or disrupt the films of oxide that insulate the globules of zinc from each other and to aid the coalescing of these particles into pools of liquid zinc. The action is not complete, but about 65 per cent of the original weight of dross is recovered as metal in this operation. The treated dross still contains metal that is recoverable by screening and disintegrating. The dross-screening equipment consists of a vibrating screen in closed circuit with a hammer mill and elevator. The vibrating screen is fitted with two screens, the upper one of heavy wire and ¼-in. mesh serving to protect the lower one from abrasion by the heavier particles of zinc and dross. The under screen has 16 meshes to the inch and the wire is 21 gauge, the screen aperature being 0.0275 in. square.

The cooled dross is tipped onto the screen through a 1-in. grizzly and is treated in batches. The undersize from the screen falls into a push conveyor, where it is wet by sprays to prevent dusting and is delivered into trucks for transport to the feed bins of the final roasting furnace. The oversize from both screens passes to a hammer mill, where dross particles are broken, and then by means of the elevator back to the head of the screen. The material is circulated until practically all dross particles are broken and removed, leaving clean prill metal, which is finally discharged into trucks and returned to the melting furnaces. This amounts to 1.5 to 2 tons per day, equivalent to 0.75 to 1.0 per cent of the weight of cathodes melted.

The screen and elevator are connected to a fan, which delivers dust into the baghouse. The baghouse is divided into two sections, one of 96 bags in 8 rows of 12 receives the flue gases from the furnaces, while the other of 48 bags in 4 rows of 12 receives the gases from the dross hoods, dross-mill housing and dross-screening plant. The bags are of flannel, each 30 ft. long, with 150 sq. ft. of filtering area. The bottoms of the bags open into a mild-steel hopper fitted with a screw. There is one hopper for each double row of bags.

The flue from the furnaces is sufficiently long to allow the gas to cool to below 110° C. before entering the first section of bags. The volume is 30,000 cu. ft. per minute and the filtering rate about 2.1 cu. ft. per minute per square foot of bag area. The bags are shaken by hand twice each shift. The pressure before shaking rises to about 2.5 in. water gauge and drops to 0.5 in. after shaking. The material caught is a black mixture of unburned carbon and zinc oxide carrying 42 per cent zinc and amounting to 750 lb. per day. The gas to the other section is relatively cool and amounts to 11,000 cu. ft. per minute. The filtering rate is 1.5 cu. ft. per minute per square foot bag area. The pressures before and after shaking are 1.5 and 0.5 in. water gauge, respectively. About 5000 lb. of dust is caught per day, with a zinc content of 75 per cent. The chlorine content of the mixed dust is approximately 1.8 per cent.

Once a day the hoppers are emptied by means of the screws, which deliver into a small bin or hopper from which the dust is conveyed pneumatically to the combustion chambers of the final roasting furnaces, where the carbon is burnt and the chlorine eliminated.

Zinc is tapped from the crucible into a cast-iron pouring pot of about 600-lb. capacity, the taphole being stopped with clay when the pot is full. The pot is held by a chain block to a crawl on an overhead runway leading to the mold bench. One pot and runway serves each furnace and one side of the mold bench. One pot fills 10 molds.

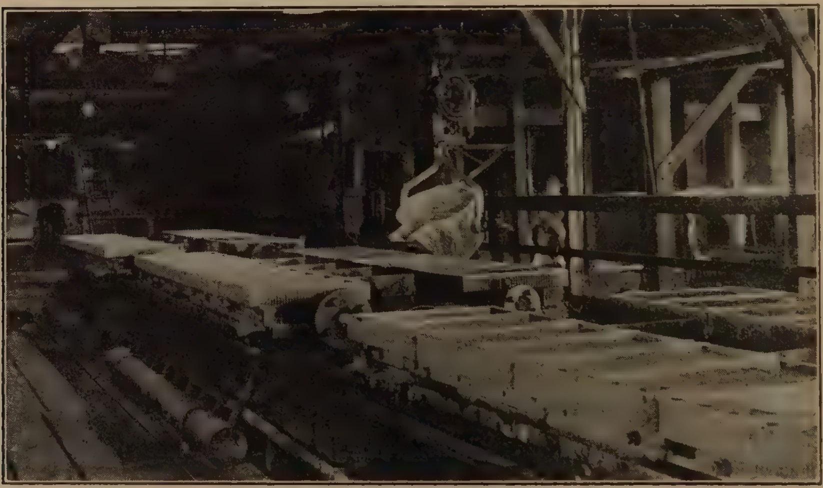


FIG. 15.—MOLD BENCH.

The mold bench for high-grade zinc consists of two parallel rows of 30 molds each. The molds are pivoted on a shaft and are tipped by hand in batches of five (Fig. 15). The molds are $18\frac{7}{8}$ in. long, $9\frac{1}{4}$ in. wide and $1\frac{5}{8}$ in. deep. They are fluted on the under side to facilitate cooling, which is further assisted by a blast of low-pressure air (0.75 lb. per sq. in.) at the rate of about 50 cu. ft. per minute per mold.

As the molds are filled they are skimmed with a mild-steel rake to remove scum, and when the zinc has solidified, which takes from 3 to 5 min., they are tipped. The slabs fall onto a chain conveyor underneath. The chain conveyors from each line of molds deliver the slabs down mild-steel slides to a common roller conveyor feeding a timing wheel, or spacer, which lifts the slabs and places them between spurs on a chain conveyor 550 ft. long, leading down to the foreshore. They are taken from the conveyor by hand, inspected, and stacked in two heaps of 60 slabs each (20 high, 3 base) on a steel truck, weighed and put into storage or taken to the wharf for shipment.

On the wharf each stack is lifted by a chain block and a special cage to fit the stack, deposited on a stacking frame and is ready for lifting into ships' holds by means of a cage specially designed to take two stacks. These are handled by the wharf cranes.

A portion of the zinc is sold as leaded zinc containing 0.85 to 1.0 per cent lead, which is added to molten zinc in a mixing furnace of the reverberatory type. The dissolution of the lead in the zinc is assisted by agitation with air. Samples of zinc are taken from this furnace three times per shift and the lead content determined within 30 min., and on these results any necessary adjustments of the lead addition are made.

Temperature variations in this furnace are undesirable, because when the temperature drops the lead content of the zinc drops and when the temperature rises the separated lead is apt to be picked up in excessive quantity. The safe working range is from 460° to 480° C.

The metal from this furnace is tapped in a manner similar to that used with the larger furnaces, and is poured into molds of a distinctive shape. The slabs are delivered to the wharf in the same manner as the high-grade metal.

A small amount of dross forms in this furnace and is drawn off and screened by itself in the dross-screening plant. The metal prills recovered are melted in the leaded zinc furnace, so as to avoid contamination of the high-grade zinc with lead. Zinc at the temperature of casting has a corrosive action on pots and molds.

Pots are protected by washing them with a slurry of borax and fire clay and drying over a fire before using. This is done each shift. The life of a pot varies from a few weeks to a few months, but is usually three to four months. The place of failure is the area struck by the zinc flowing from the taphole spout.

Molds for high-grade zinc are good for approximately 1000 tons each and those used for casting leaded zinc for about 500 tons each.

Zinc dust, chiefly required for purification of zinc solution, is manufactured and a certain portion of it is sold. Defective slabs and zinc from the dross mill are used for this purpose. The slabs are melted in a small hand-fired reverberatory furnace holding about 12 tons. Zinc is tapped from this furnace into cast-iron pots and then transferred to two graphite crucibles, holding about 1000 lb. each, heated with a coal fire. The zinc runs from these through a ⅛-in. orifice in the bottom and is disintegrated by means of a horizontally directed jet of warm dry air at 190 to 200 lb. pressure.

The dust is collected in a settling chamber, withdrawn by means of a screw conveyor to a belt conveyor rising above two trommels, one over each of two storage hoppers. From these the dust is taken in side-tipping trucks to the leaching division as required. The settling chamber and trommels are connected to an exhaust fan, which delivers the dust-laden air through a modified cyclone to a baghouse provided with calico filter bags. The blowing rate is 400 to 450 lb. zinc per hour per pot and the temperature in the blowing pots is held at approximately 500° C. The coarse dust used in purification is of 50 per cent minus 200-mesh, while the dust collected in the baghouse is of 95 to 97 per cent minus 400-mesh. The latter product is sold to cyanide plants for gold precipitation.

TABLE 6.—*Melting Data*

AVERAGES PER FOUR-WEEKLY PERIOD FOR 11 PERIODS TO APRIL 29, 1936

	High-grade Section	Leaded-zinc Section
Cathode zinc melted, tons	5,673	
Proportion of scrap therein, per cent	3.84	
High-grade zinc produced, tons	5,444	
Molten zinc from high-grade section, tons		1,908
Lead used, tons		17
Leaded zinc produced, tons		1,900
Dross and baghouse dust produced, tons	288	30
Assay of dross and baghouse dust, per cent:		
Zinc	77.9	78.0
Lead		1.9
Metal recovery, per cent	95.97	98.70

	High-grade Section	Leaded-zinc Section
Metal in dross and baghouse dust, per cent of feed	3.95	1.23
Unaccounted loss, per cent of feed	0.08	0.07
Coal consumed: tons	505	50
Per cent of feed	8.91	2.59
Ammonium chloride used, lb	10,212	582
Lb. per ton feed	1.80	0.30
	High-grade Zinc, Per Cent	Leaded Zinc, Per Cent
Average analysis of products:		
Zinc	99.9760	99.0824
Lead	0.0148	0.9070
Copper	0.0008	0.0008
Cadmium	0.0072	0.0072
Iron	0.0012	0.0026
Arsenic	<0.00001	<0.00001

ACKNOWLEDGMENTS

The author desires to express his appreciation to the Directors and Management of the Electrolytic Zinc Company of Australasia Ltd. for permission to publish this paper.

Electrolytic Zinc Plant of the Sullivan Mining Company

By W. G. Woolf,* Member A.I.M.E., and E. R. Crutcher†

The electrolytic zinc plant of the Sullivan Mining Co. is in Government Gulch, at Silver King, Shoshone County, Idaho, in the Coeur d'Alene mining district, about one mile from the Bunker Hill smelter and about three miles from Kellogg. The Sullivan Mining Co., which owns both the zinc plant and the Star mine, is itself owned jointly by the Bunker Hill & Sullivan Mining & Concentrating Co. and the Hecla Mining Company.

The Tainton high-density, high-acid process is used at this plant, therefore some parts of its flowsheet differ markedly from those of electrolytic plants using the low-density process. While it is a custom plant and has treated a variety of zinc concentrates originating from various sources in a number of states, it has obtained its main supply of zinc concentrates chiefly from the zinc-bearing ores of the Coeur d'Alene mining district, of which the principal important sources have been the Bunker Hill and Star mines. Thus the main feed has been zinc concentrates obtained from complex lead-zinc-silver ores. For the year of 1935 the concentrates had the following composition: water, 9.5 per cent; Zn, 50.6; Pb, 3.3; Fe, 9.4; S, 31.0; Cu, 0.2; insoluble, 2.9.

Flowsheet

The concentrates are delivered to the plant in railroad cars, which discharge into storage bins directly under the track. Bottom-dump cars are dropped directly into the bins while a slip scraper, pulled by an air tugger hoist, is used to empty box cars. There are five storage bins for concentrates, each of approximately 300 tons capacity. At the bottom of each bin there are individual belt feeders that discharge onto a common conveyor belt, which in turn discharges to another belt that carries the concentrate onto a weightometer belt for weighing. Immediately after the weighing, the crushed oversize return from the roasters is added to the load on the belt and then the ground-up sweepings, lumps and roaster cleanings. An electromagnet at the end of this conveyor removes tramp iron from the feed. The belt discharges to a set of 30 by 12-in. rolls, which break up lumps or frozen chunks of concentrate, etc. Beneath the rolls there is a screw conveyor, which conveys the roll discharge to a

---

Manuscript received at the office of the Institute Oct. 6, 1936.

* Superintendent, Electrolytic Zinc Plant, Sullivan Mining Co., Kellogg, Idaho.

† Assistant Superintendent.

bucket elevator into which a separate screw conveyor feeds flue dust and Cottrell dust.

The elevator raises the feed to the tripper floor, where a conveyor with tripper distributes the feed to any one of five roaster-feed bins, one for each roaster. The feed bins have a capacity of about 25 tons each, sufficient for somewhat more than 12-hr. supply for each furnace.

The five roasters installed at the plant are 25-ft. dia. Wedge roasters with seven hearths below the drier hearth. Feed is supplied to the furnace by scrapers attached to the rabble arms, which scrape the concentrate off a shelf comprising the bottom of the feed bin. A more or less constant feed is fed to the furnace at each revolution of the arms and this amount may be increased or decreased by adjusting the length of the scrapers. At full plant capacity, normally four roasters are operated at one time, the fifth being held as a stand-by.

Each of the hearths on the roaster has two air-cooled rabble arms and on hearths 3, 4, 5 and 6 there are also two air arms, which distribute the air that has been used to cool the rabble arms, and which has itself thus become heated. An arrangement of valves permits the preheated air from the rabble arms on hearth 6, for example, to be distributed over hearth 5 through a series of ¾-in. holes along the entire length of the air arms. The air can only be distributed on the hearth next above the one on which it was used to cool the rabble arm; thus, air from hearth 5 can be distributed on hearth 4, etc. If desired, any portion or all of the cooling air may be released to the atmosphere instead of being used in the furnaces.

Air to cool the rabble arms is supplied by a blower from each furnace, direct-connected to a 15-hp. motor, and draws air from outside of the building.

Each roaster is driven by a 10-hp. motor belted to a gear-reduction unit, connected through a pinion and ring gear to the central shaft, which in turn carries the rabble arms and the air arms. In the couplings between gear reduction and the pinion, two shearing pins are used as a safety in case the shaft becomes stalled.

Each roaster is equipped with two Mahr-type oil burners on the bottom hearth. Portable burners may be placed at need on any hearth. This is particularly necessary when warming up a furnace at the time of starting. For every two Mahr burners there is a fan, direct-connected to a 7½-hp. motor, which supplies the air needed for the Mahr burners. Fuel oil of about 29° Bé. is used.

The roasted calcine is discharged at the periphery of the bottom hearth through a chute to a Jacoby conveyor. In the chute there is a grizzly which removes any lumps of calcine too coarse to be carried through the conveyor. The chutes also have a by-pass, which permits improperly roasted calcine to be dropped on the floor and eventually returned to the roaster feed.

The Jacoby conveyor is a cast-iron tube, 14 in. in diameter, mounted on tires which in turn ride on trunnions. Inside this tube and cast integral with it, there is a helical screw. The entire conveyor is rotated and thus the calcine that has been dropped into the tube is carried along it by means of the screw, and in traveling through about 150 ft. of conveyor is cooled from approximately 400° C. to about 100° C. Since the proper design of roller was developed and installed for use in this conveyor there has been very little upkeep cost in connection with it and its operation has been most satisfactory.

The calcine discharged by the Jacoby conveyor is elevated by a bucket elevator to a calcine storage bin, from which it is drawn as needed and elevated to pass a vibrating screen of about 8 mesh. The oversize from the screen is crushed and returned to the roaster feed, as previously described. The undersize is conveyed by screw conveyors to the five main calcine storage bins, from which it is drawn to the leach weigh hoppers, as required. Each calcine-storage bin has a capacity of approximately 170 tons.

Roaster gas from the Wedge roasters is discharged through two uptakes connected to the top hearth on each roaster. The uptakes are provided with clean-out doors to allow for the removal of accumulated dust and accretions. From the uptakes the gas enters a balloon flue about 1100 ft. long, which connects the roaster building proper with the Cottrell treater plant. The Cottrell treater and stack are on a hill about 400 ft. above the roaster building. At intervals throughout the length of the flue are dust gates through which any material settling out is drawn into cars and returned to the roasting plant for re-treatment. The solids that are too fine to settle out in the flue are recovered in a plate and wire-type Cottrell treater. From the treater, gases enter the base of the stack, which is 14 ft. in diameter and 250 ft. high. With a few exceptions, extremely good clearance of the stack is maintained at all times.

The flue dust recovered has averaged about 10 per cent of the raw concentrate; Cottrell dust about 4 per cent. However, as the milling practice has trended toward finer grinding, a zinc concentrate of finer mesh has been produced, so that the percentage of roaster flue dust has been increasing. The flue dust, and more particularly the Cottrell dust, are difficult to handle, as at times they flow very much like water and thus rush out through a small opening in any type of feeder.

Samples of flue dust and Cottrell dust have given the following range of assays:

	Zn, Per Cent	Acid-soluble Zinc, Per Cent	Water-soluble Zinc, Per Cent	Iron, Per Cent	Sulphur, Per Cent
Flue dust	43–49	25–40	7–12	6–9	1–12
Cottrell dust	20–45	15–25	9–20	2–7	2–12

All flue and Cottrell dust is returned to the roasters.

The main object of the roasting operation, of course, is to render soluble as much as possible of the zinc in the returned sulphuric acid electrolyte, which is used for leaching. Since a dead roast can be obtained only by an increased degree of heat, which in turn increases formation of ferrites, and since any sulphide sulphur left in the calcine will tie up approximately twice its weight of zinc, the most efficient roast demands rather a nice balance between sulphide sulphur left in the calcine and ferrite produced in the calcine. Another factor that enters into the roasting operation involves the necessary replacement of soluble-sulphate losses from the plant in leach residues, purification residues and other unavoidable solution losses. These must be replaced by the formation of zinc sulphate in the calcine during the roasting operation. It is therefore necessary to roast to a low-sulphide sulphur, to a sufficiently high water-soluble zinc, and to as low a ferrite formation as possible. In order to avoid formation of ferrite, a maximum temperature of 750° C. on any floor has been set. Individual roasters in this plant have at times handled as much as 65 wet tons of concentrate per furnace for 24 hr., and we have also kept the furnaces alive with as little as 18 tons per furnace for 24 hr. The most economical rate for the present grade and type of concentrate feed appears to be between 40 and 50 tons of wet concentrate per 24 hours.

Roaster operators determine the sulphide sulphur in the calcine two or three times each shift and water-soluble zinc is also determined frequently. Methods have been worked out and equipment supplied so that the roaster operator himself makes these determinations in a laboratory provided on the roaster floor. Much better operating results have been obtained since this practice was introduced.

For the year 1935 the average calcine analysis was as follows: total zinc, 56.0 per cent; laboratory "acid-soluble" zinc, 50.7; water-soluble zinc, 3.4; total sulphur, 3.1; sulphide sulphur, 0.47; iron, 9.2; insoluble, 4.1.

Leaching Department

Calcine is delivered to the leaching department from the calcine-storage bins, previously referred to, by means of a mechanical feeder in the bottom of each bin, which discharges through a series of conveyors and elevators to two calcine weigh hoppers over each of three agitator tanks. In addition to the calcine weigh hoppers there is also a manganese dioxide weigh hopper over each agitator.

The leach agitators are 20-ft. dia. by 13-ft. stave lead-lined tanks. The agitators in these tanks consist of an iron shaft supporting a radial arm just above the solution level in the tank. Lead-covered, extra heavy hydraulic iron pipes, 3 in. inside diameter, are fastened to this radial arm and extend vertically within 4 in. of the bottom of the tank. Each two adjacent pipes are joined by heavy cast-iron lead-covered shoes at the bottom. As the drive shaft rotates, the radial arm and the fingers attached to it also rotate and keep even a heavy pulp in thorough suspension.

The batch system of leaching is used in this plant. A measured amount of returned electrolyte is pumped into the leaching tank and, if it has not been previously heated, it is now heated to about 60° C. by means of process steam through lead steam coils installed in the tank. Two-thirds of the estimated requirement of calcine for complete neutralization of the acid is then added. Agitation is continued for a period of 3 to 5 hr., depending upon the time available for the completion of the leach. A very good extraction is obtained on this portion of the calcine, since the minimum acid strength in which it is leached is from 40 to 60 grams per liter. During this stage of the leach the chemical reaction between the zinc oxide of the calcine and sulphuric acid develops sufficient heat to bring the entire leach to the boiling point. The recording thermometer in each tank indicates this temperature to be from 104° to 106° C., depending on the specific gravity of the solution.

The remaining acid in the solution is then carefully neutralized by adding small weighed additions of calcine. The leach is then reacidified to about 20 to 25 grams of sulphuric acid per liter by the addition of more returned electrolyte. The acid is again carefully neutralized to avoid addition of excessive calcine over that required to neutralize all acid and precipitate practically all of the iron. This double leach or repeated reacidification step is resorted to in order to improve the filterability of the pulp. At times there is also added approximately one pound of glue per ton of pulp, which very definitely improves filtration.

Iron taken into the solution in the leach varies from 12 to 25 grams per liter, depending on the roast and the iron content of the calcine being treated. At the end of the leach the iron does not exceed 25 mg. per liter in the solution. Manganese dioxide is added as required to oxidize any ferrous iron present so that it will be precipitated as ferric hydrate or basic iron sulphate.

The tanks are discharged through 6-in. lead pipes into a semicircular wood-stave launder through which the pulp flows to a lead-lined storage tank ahead of the Burt filters. Very satisfactory service has been obtained from these semicircular launders. The pulp is delivered from the storage tank to the Burt filters through 6-in. copper pipe.

There are six Burt filters, each 5 ft. in diameter and 40 ft. long. The shells are of steel lined with copper. The pulp to be filtered, all wash water and also compressed air for supplying the pressure for carrying on the filtration are all admitted through the hollow trunnion at the head end of the filter. Inside the filter shell there is a series of canvas-covered, riffled or fluted wooden filter boards, lining the inside circumference of the shell. There is a pipe connection through the shell from each filter board, which discharges the clear solution and wash waters into the separate sumps. The solid from the pulp is collected on the canvas, forming a cake on the surface of the filter boards. As it enters the Burts the pulp is about 85° C., and although the resulting filtered solution is neutral, all equipment for handling both the hot pulp and the hot solution must be resistant to copper sulphate corrosion. An average filter cycle is about as follows:

The filter is first filled almost completely with pulp, the valve closed, and the filter started rotating. Then 35 lb. of air pressure is admitted through the hollow trunnion to the inside of the filter, which forces the solution through the canvas and out through the discharge nipples of each individual filter board. After the solution is thus all filtered from the pulp, three successive washes of gradually decreasing zinc sulphate content are added, each successive wash being forced out completely before the next one is added. By this means the soluble zinc content remaining in the cake is reduced to a satisfactory amount. When the washing is completed, vacuum is applied to the interior of the filter, drawing the air from the outside through the solution discharge nipples and causing the cake to drop off the canvas filter cloth. Water is then run in and the filter is rotated until the residue is entirely mixed with water to form a slurry. Discharge ports in the end of the filter are opened and the repulped cake or slurry is permitted to discharge by gravity from the filters through a series of launders to two Dorr thickener tanks. The overflow from the thickeners goes to storage and is again used for repulping the residue in the filters.

The underflow from the Dorr thickeners passes to one of two 10 by 12 Oliver vacuum filters. The cake from the Oliver filters is conveyed by means of a belt conveyor to a Ruggles-Coles drier, which reduces the moisture content so that the moisture of the dried residue is from 15 to 20 per cent. The dry product is loaded into railroad cars and is shipped to the Bunker Hill lead smelter, where it is treated for the recovery of its lead, silver and gold contents.

The filtrate from the Burt filters is pumped through hoses to a lead-lined storage tank, from which it is drawn by gravity to the purification department as required.

The life of the canvas filter cloth in the Burt filters varies from 30 to as much as 90 days and the wooden boards themselves last a year to a year and a half.

In the operation of the filters it has been found more economical to change all the clothes in a filter at one time. There are 32 separate filter boards in each filter, each one inside its canvas sack, and as a leak appears in any board, the nipple corresponding is plugged with a wooden plug. When from 10 to 15 nipples in a filter are plugged, it is more economical to change all sacks than to continue operating at reduced capacity. The discharge head of the filter is therefore taken off, all boards removed, and a set of filter boards with new canvases on them are installed. By the use of 60° triangular boards, which were a development of this plant, the filter capacity has been practically doubled.

A filter cycle requires from 3 to 4½ hr. to complete and the quantity of pulp charged to the filters is varied as necessary to give this figure. A filter with a new set of sacks has a capacity as high as 130 tons of pulp per 24 hr. and when, owing to increasing age of the canvas sacks, the capacity has dropped off to 75 tons for 24 hr. or even less, a new set of sacks is required.

This type of filter is very satisfactory for the particular work in this plant. We are dealing with a hot (80° C.) pulp and with a zinc sulphate solution that is almost saturated at this temperature. If a vacuum filter were used, there would be an almost instantaneous crystallization of zinc sulphate, which would blind the canvas and prevent filtration; also, since the solution is so concentrated, washing must be thorough and complete in order to avoid excessive soluble losses of zinc in the residue. The amount of new wash water that can be used in the cyclic operation is limited by the amount of water evaporated throughout the process, in the leach agitators, etc., consequently efficient use must be made of the amount of wash water it is possible to add.

Purification Department

Zinc sulphate solution produced in the leaching department contains, in addition to the dissolved zinc, a number of impurities, chief among them being copper, cadmium, cobalt, antimony, arsenic, nickel and germanium. There are other minor impurities, some of which are not injurious to electrolysis. This solution contains approximately 215 grams per liter of zinc, 300 mg. per liter of copper, 600 mg. per liter of cadmium, 15 to 30 mg. per liter of cobalt, 3 to 8 mg. per liter of antimony plus arsenic; also manganese and magnesium, which do not have to be removed from the solution in the purification step.

The solution is drawn from storage tanks through 6-in. dia. copper pipes, fitted at their discharge ends with rubber hoses and pinchcocks instead of valves, to lead-lined tanks, 22 ft. in diameter by 15 ft. high, which contain mechanical agitators of the paddle type. The agitation required for purification is not as violent as that required for the leaching operation. The tanks are fitted with lead-pipe steam coils and can be heated by process steam, so that the solution temperature can be raised if necessary to obtain more efficient precipitation of impurities by means of zinc dust.

A charge of solution is drawn into one of the agitators and sufficient zinc dust added to precipitate all copper in the solution. This charge is then filtered through Shriver plate-and-frame filter presses and is discharged into another agitator similar to the one in which the copper was removed.

The removal of cobalt is aided by the presence of only a small amount of copper in the solution. For this reason a small amount of raw solution is drawn from the storage tanks and mixed with a larger bulk of solution from which the copper has already been removed. The temperature of the solution is now held at 75° C. or slightly above, and more zinc dust added to the agitator until cobalt, antimony and cadmium are reduced to one milligram per liter or less. When the cobalt is precipitated, the nickel is also removed, and for that reason the operators do not test the solution regularly for nickel.

Also, while a little copper present in the solution is beneficial in precipitating cobalt, a larger amount is objectionable. In tests we have succeeded in precipitating all copper and cobalt in one tank with a reasonable amount of zinc dust; however, before the solution could be filtered, the precipitated cobalt redissolved in the solution. For this reason the step-purification outlined is used.

The final filtrate from the Shriver presses is a clear, water-white solution containing about 215 grams per liter of zinc, and less than a milligram of cobalt, antimony and cadmium. This solution then passes to a storage tank called a "check" tank. Analytical tests have been developed, which the operators, who are ordinarily not trained chemists, regularly make. These methods are quick, accurate and very sensitive. To be absolutely sure, however, that the solution is pure, a sample is taken of each charge by an automatic sampler during the final filtration into the storage tanks, and this sample is sent to the laboratory for regular routine analysis. Before the solution can be used by the electrolytic department, approval of that particular batch of solution must be obtained from the laboratory.

The residue obtained from this zinc-dust purification contains copper and cadmium in commercial quantities, also some cobalt, antimony, nickel, etc. The residue is re-treated in the cadmium plant for the recovery of copper and cadmium. As produced, this residue contains from 25 to 35 per cent Zn, from 8 to 10 per cent Cu, and from 16 to 22 per cent Cd.

The filter medium used in these presses is ordinary 10-oz. canvas duck. In order to get a clear, sparkling filtrate, paper is also used over the canvas. The paper that has been found most satisfactory is an ordinary 30-lb. Kraft paper such as is used extensively for wrapping parcels. When the press is opened for cleaning, the papers are peeled off the canvas, leaving little or no residue on the cloths to be washed off. Disposal of the paper is a simple problem, as it is merely thrown into the leach agitators, where it readily disintegrates.

ELECTROLYTIC DEPARTMENT

In the cell room there are two circuits of 150 cells each, in series electrically but in parallel as regards the solution flow. Each circuit is supplied by a motor-generator set consisting of a synchronous motor direct-connected to two direct-current generators of 4000 amp. and 500 volts each, which are connected in series to give 8000 amp. d. c. The synchronous motor is operated at 2300 volts and is rated at 4400 kilovolt amperes. Current density is approximately 100 amp. per sq. ft. of submerged cathode area.

app
? w

Each cell contains 12 cathodes and 24 anodes. Electrodes are held in place in the cells by lead-covered wooden frames, which are wedged in place in the cells. The guides for the cathodes are of wood, impregnated with paraffin. The cathodes slide in these wooden guides. They also serve as spacers for the anodes, which are held in position against the side of the guides. Thus a regular spacing between anodes and cathodes is maintained. The distance between anode and cathode face is only 5/8 in., therefore the spacing must be kept uniform in order to avoid treeing and consequent low efficiency. The wooden guides are replaced about every 60 days.

Cathodes are made of 1/8-in. aluminum plates with an aluminum header bar welded to the sheet by means of the atomic hydrogen-welding process. This process was new at the time of the first fabrication of the cathodes at the commencement of plant operation, but the method was very successful and is still in use.

Since each cathode must carry several hundred amperes, a good contact at the cathode bus bar is essential. This is obtained by using a copper clip attached to the bus bar into which the header bar slips, and by the use of copper plating on the aluminum header bar itself a copper-to-copper contact instead of aluminum-to-copper is obtained. Periodically the plating on the header bars is renewed. The clips and header-bar contact are on one side of the cell, so that there is no exposed copper over the cell proper.

Cells are not cascaded, but are set up in two rows of 75 cells each in each circuit. The cells are side to side instead of end to end, as is general practice in plants using the cascade system. The 1 by 2-in. copper bars that connect the pairs of cells are supported independently of the cells. These bars act as the cathode bus for one cell and the anode bus for the cell adjoining. Copper tie-up, therefore, is relatively small for the amperage carried in the circuit.

Solution is circulated continually through the cell at a rate of approximately 10 gal. per minute per cell. The overflow from the cells drops into the sumps through hard-rubber pipes. There is a sump directly beneath each row of cells extending the full length of the row. This sump is large enough to hold all of the solution from all of the cells above it if it becomes necessary to drain the cells because of a long power interruption. From the sumps the solution goes to lead-lined launders and storage tanks, which in turn feed hard-lead pumps delivering the solution to the cooling cells, which are high enough to permit a gravity flow of solution back to the electrolytic cells.

There are five cooling cells, each containing sixty-six 1½-in. lead-pipe coils through which cold water is circulated. The electrolyte is circulated through the cells and around the coils containing the cold water. They are in series as regards solution flow but are in parallel for water flow. A total of approximately 3000 gal. of water per minute is circulated, or about 600 gal. per cooling cell.

The neutral solution is delivered to the cell building as required, through an iron launder, from which it discharges into a lead-lined launder inside the building, which in turn discharges into an electrolyte storage tank. Electrolyte is pumped back to the leaching department through lead-lined iron pipe by Antisell lead centrifugal pumps. This neutral solution is fed to the cell circuit in batches, instead of continually, as is general practice. As an example—assume that the acid in the circulating cell-room electrolyte has reached 27 to 28 per cent sulphuric acid, a volume portion, say, ⅕ of the circuit volume of this solution, is pumped from the cell room to the leaching department and an equivalent amount of neutral solution is drawn from the purification storage tanks to the cell-room circuit. This reduces the acid in the electrolyte to approximately 22 per cent. Electrolysis is continued until the circuit is again up to 27 per cent acid, whereupon the above cycle is repeated. Since the zinc content of the neutral solution is much higher than is in general use in electrolytic plant practice, a relatively small tonnage of solution is required to produce the zinc. Approximately 5½ tons of solution per ton of zinc cathodes produced is the amount required.

Cathode deposits from 8 to 12 hr. old are made, depending on plant and solution conditions. When withdrawing plates from the cells for stripping of the deposited zinc, only one cathode is pulled at a time and a clean cathode immediately inserted in its place. After draining, the cathodes are loaded on a truck and hauled to the stripping floor in another room, where the actual stripping is done.

By the use of reagents a froth is maintained on the solution in the cells at all times, which prevents mist or gas in the cell-room atmosphere. No masks or respirators are required even for men working in the cell room continually. All men working around the cells are required to wear rubber gloves and boots as a protection against acid contact or electrical shock.

The cells themselves are lead-lined, wooden boxes. The general cell-room construction has worked out well in practice and has given good service.

Anode and cell boxes are cleaned of the precipitated manganese dioxide periodically by a crew working continually at this particular task.

Cathode zinc from the stripping operation is piled on trucks in piles of 700 or 800 lb. each, six such piles forming a truck load. The loaded trucks are delivered to the melting and casting department after being weighed.

Melting and Casting Department

Cathodes are melted in a coal-fired reverberatory furnace, 15 by 28 ft., with inverted arch hearth. There are two ladling wells in the end of the furnace opposite the firebox, separated by a bridge wall from the main metal bath. These wells are oil-fired to maintain the metal at the proper temperature for casting.

The furnace holds approximately 100 tons of molten metal in the bath. Molds for standard slabs, or for special shapes as required, are set in a line reached by the ladle, which is carried on a crawl suspended from an I-beam. The ladle, handled by one man, carries from 350 to 400 lb. of molten metal.

Cathodes are raised by an electrically driven traveling chain hoist from the floor level to the charging level above the furnace. The cathodes are picked up in piles weighing 700 to 800 lb. each and are raised to the top of an inclined metal chute, down which they slide through an opening in the top of the furnace into the molten metal beneath. A swinging door over the opening in the furnace prevents excess air from entering during the charging operation.

The furnace is drossed after 60 to 75 tons of cathodes has been melted. Once or twice each month wall and arch accretions of dross are barred down.

Special care is taken to avoid contamination of the metal. Scrap, skimmings and cleanings from around the furnace and molds are melted in a separate furnace and converted into zinc dust instead of being returned to the main furnace.

Since the metal produced by this plant is all of "Special High Grade," according to the specification of the American Society for Testing Materials, great care is taken to obtain accurate analyses. A sample of the metal being cast is taken from each ladle of metal and poured into a mold that produces a small, round stick. When a lot is completed (about 50 tons) all of the stick samples taken during the casting are melted carefully in a clean graphite crucible, being thoroughly stirred. The molten sample of the metal is granulated by pouring it in a thin stream into distilled water, then is taken to the laboratory for analysis before that particular lot is released for shipment.

Slabs are loaded with hand trucks into box cars for shipment as required. Each truck load of metal is weighed over two shipping scales, a separate weighman being at each scale. The weights obtained by the two weighers must be in accord before the car is sealed for shipment.

Dross formed in the melting of the cathodes is sold and is not re-treated in the plant.

Zinc dust for use in the purification department and in the cadmium plant etc., is produced in the usual manner by atomization of a small stream of molten zinc with a high-pressure air jet. Oversize dust, scrap and any metal that may have become contaminated in any way is used for the production of zinc dust.

Electrolytic Cadmium Plant

Purification residue, obtained by the precipitation of impurities by means of zinc dust in the purification department of the zinc plant, as previously described, is sampled, weighed, and is then stored in outside storage bins for re-treatment in the cadmium plant. This residue is carried by conveyors from the storage pile to a storage bin in the cadmium plant. From the bin it is fed as needed by an adjustable feeder into a ball mill to which a small amount of water is also fed for the purpose of breaking up lumps and producing a fine sludge. The sludge from the mill is carried by means of a lead-lined launder into a lead-lined leaching tank, where it is agitated with spent electrolyte return from the electrolytic cells of the main zinc plant. Cadmium, etc., is dissolved, leaving the copper in the form of cement copper, which is eliminated at this step. The pulp in the tank is filtered through a bronze Shriver plate-and-frame press. The press cake is dropped into a storage bin and is shipped at intervals to a copper smelter.

The solution carrying the cadmium, besides other metallic impurities, is pumped to a lead-lined wooden tank similar in construction to the purification agitator tanks in the main zinc plant. Zinc dust is added for the precipitation of the cadmium as a metal sponge. The contents of the precipitation tank is filtered through a bronze Shriver filter press, and the solution is pumped to a storage tank. The cadmium sponge is placed on a platform heated by steam, where it is oxidized in a short time. The oxidized sponge dissolves readily in the returned electrolyte from the cadmium cells. All of the cadmium is not oxidized and the remaining metallic portion serves to remove small quantities of copper that may have escaped the leach; it also tends to keep other impurities from building up to their full extent in the solution. After being dissolved, the cadmium, in the form of neutral solution, is sent to a storage tank and is ready for electrolysis. The cells are of the stationary cathode type and in most respects are similar to the standard cells used in the zinc plant. However, a much lower voltage and lower current density are used in the cadmium cells. The current density is about 10 amp. per square foot of cathode surface. Cadmium electrolyte is circulated through the precipitation cells in much the same manner as in the electrolysis of zinc. At intervals, the spent electrolyte is returned to the resolution tank, where the acid generated during electrolysis is used to again dissolve cadmium sponge and the solution is returned to the cells as neutral solution. Although the electrolysis is not very sensitive to impurities, after these have built up for some time it is advisable to discard it. This is done by using it instead of zinc-plant electrolyte for leaching purification residue, the purification step being satisfactory for the elimination of the undesirable impurities.

The solution from the filtration of the precipitated cadmium sponge is purified in a lead-lined tank fitted with mechanical agitation. Purification is accomplished by means of zinc dust in a manner similar to that used in the main zinc plant. After purification, the solution is again filtered; the Shriver press cake containing the accumulated impurities is stored and the solution is returned to the main zinc-plant circuit.

Cathodes are stripped of the deposited cadmium every 12 hr. The cathode sheets are rolled in compact bundles and dried on steam racks. The bundles are pressed under a hydraulic press and then are ready for melting.

The melting of the cathode cadmium is done in an electric melting pot fitted with thermostatic control, under a cover of fused caustic soda, to prevent excessive drossing of the metal. Molten cadmium is cast into shapes required by the market—pencils, balls, slabs or anodes. These are boxed in wooden containers for shipment to market.

The tanks throughout the cadmium plant are lead-lined and equipped with steam coils to permit temperature control of the solution at any stage of the process. A separate motor-generator set supplies the cadmium plant with its own source of direct current independent of the zinc-plant generators.

The entire cadmium plant is so arranged that any unit can be temporarily shut down without affecting the operation of the rest of the process. In general, it resembles the zinc plant on a smaller scale, and embodies the features of design indicated by the experience of the electrolytic zinc plant.

The Electrolytic Zinc Plant of the Consolidated Mining and Smelting Company of Canada, Limited

By B. A. Stimmel,* Member A.I.M.E., W. H. Hannay† and K. D. McBean‡

The electrolytic plant at Trail, B. C., was erected by the Consolidated Mining and Smelting Company of Canada, Ltd., for the treatment of zinc ores and concentrates, particularly those of the Sullivan mine at Kimberley, B. C. It began operations in 1916 at a rated capacity of 60 tons of cathodes per day, which has been steadily increased to the present production of 400 tons per day.

The Sullivan has furnished the greater part of the zinc so far produced, although notable tonnages of customs zinc concentrates have been treated. The maximum yearly tonnage of customs concentrates, 25,000 tons, was treated in 1926. Practically no customs concentrates have been treated since 1929. The total bar zinc production to the close of 1935 was 1,092,782 tons. The zinc mineral in the Sullivan ore is marmatite of somewhat variable composition, ranging between $6ZnS.FeS$ and $8 ZnS.FeS$. Practically all the zinc ores tributary to this plant are marmatites; and the iron content of the zinc mineral varies considerably. The formation of zinc ferrite during roasting is now a matter of common knowledge, so the possible extraction from any zinc concentrate is largely a function of the iron content; the progress made in concentration is reflected directly in zinc-plant recovery.

The Trail plant operates on the low-acid system, as do all the other major plants on this continent at present operating, except the electrolytic plant of the Sullivan Mining Co. at Kellogg, Idaho. The new Magdeburg plant, in Germany, occupies an intermediate position between high and low acid. Plant operation at Trail will be treated in this paper under five main sections: roasting, leaching and purification, electrolysis, cadmium recovery and melting. The oxide section of the plant, treating zinc fume from re-treatment of lead blast-furnace slag, is practically a separate zinc plant; this is necessary because of the presence of fluorine in the smelter zinc fume. Cadmium is recovered electrolytically from the purification residues of both the sulphide and oxide leaching plants.

Manuscript received at the office of the Institute July 3, 1936.

* Superintendent of Zinc Plant, Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C.

† Research Chemist, Consolidated Mining and Smelting Company of Canada, Ltd.

‡ Superintendent of Roasters, Consolidated Mining and Smelting Company of Canada, Ltd.

SUSPENSION ROASTING PROCESS

Since the initial conversion of a standard, 25-ft. diameter Wedge roaster to the combustion-chamber type, the development of the "burning concentrate process" has proceeded steadily, until, with the latest design, concentrate that would have been difficult to treat in the original roaster can now be handled easily.

Before the operation of the "burning concentrate process," the roasting department at the Trail zinc plant consisted of 25 standard Wedge roasters, 25 ft. in diameter, some coal fired and others operated autogenously by the so-called "split-draft" system. However, as the process evolved, and its advantages became more evident, more of the roasters were converted to the new type. Upon the conversion of the eighth roaster to the suspension type, sufficient capacity became available to satisfy the calcine requirements of the zinc plant, and all roasting by the multiple-hearth method was discontinued.

While the idea of roasting zinc concentrates in suspension has intrigued investigators for a number of years, no commercial application of a process appears to have been successful until the development of the Trail burning concentrate process.

As worked out at Trail, the system owes its success largely to a number of unique features, combined so that the functions of drying, roasting and sulphating, if required, can be carried out simultaneously in a single unit. Auxiliary equipment is provided for the recovery of waste heat and for the collection of dusts from the exit gases.

By means of this combination, each furnace or unit can treat, without extraneous fuel, zinc concentrates containing up to 11 per cent moisture, at any rate between 50 and 130 dry tons per day. The quality of the calcine produced is subject to considerable control, and may be varied within wide limits in sulphide and sulphate sulphur content. The exit gases, rich in sulphur dioxide, are at 1600° F., and from them 2 boiler hp. per ton of concentrate roasted per day may be recovered when roasting Sullivan concentrates.

These various factors have resulted in a very compact and efficient plant, and high tonnage capacities of various types of calcine can be obtained from a relatively small installation.

APPARATUS

Fig. 1 shows in diagrammatic form a typical arrangement of the apparatus: No. 1 is the furnace proper, which contains the combustion chamber 2, the drying hearths 3 and 4, the collecting and sulphide-control hearths 5 and 6, and, when required, the sulphate-control hearth 7; each hearth having arms and rabbles rotating with the central column 8. The auxiliary equipment consists of the circulating and secondary combustion air fan 9, the burner 10, the gas-circulating conduits 11, 12 and 13, the wet-concentrate hopper 14, and the dried-concentrate hopper and feeding device 15. The ball mill 16 has a feed chute and feeder 17, and an elevator 18, at the discharge end. Chute 19 conveys the low-sulphate calcine to the Jacoby rotary conveyors 20, and chute 21 receives the product from the sulphating chamber. No. 22 is the main gas outlet and 23, the gas outlet from the sulphating chamber. By means of valves, either or both of these outlets may be used. The waste-heat exchanger 24 is usually by-passed through conduit 25, unless concentrates very low in thermal value are being treated. For such concentrates, air is passed through the heat-exchanger tubes by means of the fan 34, and is delivered to the secondary air fan 9. The boiler, 26, is preferably of the vertical, water-tube type, although fire-tube boilers are also in use. From the boiler, the gases are drawn through the cyclone dust collector 27 by the fan 28 and are passed into the balloon flue 29 and thence, through the Cottrell electrical precipitator 30, to the acid plant 31. The screw conveyor 32 can return the dust products, either to the base of the combustion chamber 5, through the elevator 33, or to the sulphating chamber 7, or to the finished-product conveyor 20.

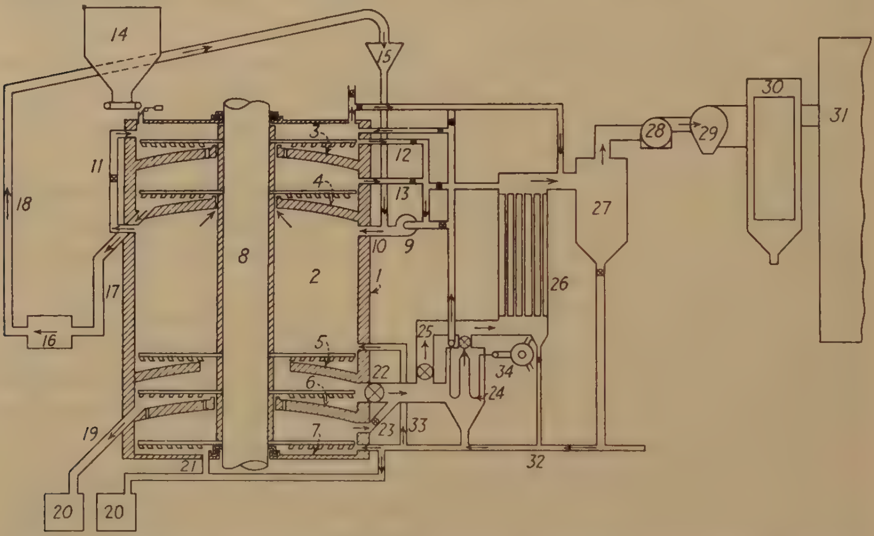


FIG. 1.—ARRANGEMENT OF APPARATUS IN TRAIL SUSPENSION ROASTING PROCESS.

PROCESS

The zinc concentrate as received from the concentrator has the following average analysis: Ag, 2.2 oz. per ton; Zn, 51.1 per cent; Pb, 3.5; Fe, 11.4; S, 32.8; Cu, 0.14; SiO_2, 0.6; Mn, 0.52; CaO, 0.2; Cd, 0.16. It contains between 9 and 10 per cent moisture.

Bottom-dump railway cars discharge to belt conveyors, which deliver to a hopper of 25 tons capacity at each furnace. By means of a belt, the wet concentrate is fed at a controlled rate through a chute—air-sealed by a gate operated by gravity—to the periphery of the first or upper drying hearth. In being rabbled across this hearth, the concentrate is partially dried by hot gases from the combustion chamber, which are being continuously circulated between the combustion chamber and both drying chambers. When the concentrate is extremely wet, the gases from the first drying chamber are not returned again to the combustion chamber but are by-passed directly to the cyclones, or exit flue system. The partially dried concentrate from the first drying hearth then drops to the second drying hearth, where it is completely dried by heat conducted through the hearth and by the circulating gases, as it is rabbled outwardly to the discharge chute. From this chute it passes to the screw conveyors, which deliver to a lightly loaded ball mill where the agglomerations formed in the drying operation are disintegrated. Practically no grinding is performed or required in the ball mill, as the concentrate normally treated at Trail is 95 per cent minus 200 mesh, which is fine enough for successful burning in suspension. After passing through the ball mill the fine, dry material is conveyed by a bucket elevator and screw conveyors to a 25-ton hopper at each furnace.

The concentrate, in a fine, dry condition, free from lumps or tramp material and at about 200° F., is now in the optimum state for the burning operation. It is fed from the hopper, by a belt feeder through an adjustable gate, into two air injectors delivering to the burner. In the burner it mixes with the secondary combustion air—which may be preheated or not, depending upon the thermal value of the concentrate being treated—and with the moisture-laden gases from the two drying chambers, and the mixture enters the top of the combustion chamber with considerable turbulence. Ignition occurs very close to the burner mouth, and the concentrate in burning maintains the temperature in the combustion chamber between 1650° and 1750° F. From time to time, as required, small adjustments are made in the ratio of concentrate to air to keep within these limits of temperature. Although there is a considerable degree of turbulence within the combustion chamber, some particles, amounting to about 60 per cent of the total feed, settle out on the collecting hearths at the base of the chamber. The remaining 40 per cent, consisting of the finer material, is carried out of the furnace with the gases into the cyclones, where almost all of the dust is precipitated.

Suspension Phase.—During the suspension phase of the operation the sulphide particles are almost completely desulphurized, and, on settling out on the hearth, contain about 0.5 per cent sulphide sulphur at normal tonnage rate. The sulphate sulphur, being fixed by the alkaline earth radicals, is about 0.4 per cent at all capacities. Upon being rabbled across the two collecting hearths, the residual sulphide sulphur is further oxidized, and when the material is discharged from the furnace it contains, on the average, about 0.3 per cent sulphide sulphur and 0.4 per cent sulphate sulphur.

At Trail this product is finished calcine, which is discharged into the Jacoby rotary conveyors and conveyed to the leaching plant. Under different plant conditions, where high-sulphate sulphurs might be desired, this calcine would be treated in the sulphating chamber by discharging from the second collecting hearth to the periphery of the bottom hearth. Here it would be rabbled in a strong sulphur dioxide atmosphere, obtained by diverting over this hearth a sufficient volume of gases from the combustion chamber to maintain the temperature at about 900° F. Under these conditions the material would rapidly build up in sulphate sulphur and the finished product would then be discharged from the furnace, containing up to 4 per cent sulphur as sulphate sulphur.

Burning.—During the burning operation, gases are being continuously circulated between the combustion chamber and the two drying chambers. These gases, at 1700° F., and from 9 to 10 per cent sulphur dioxide, are withdrawn from the top of the combustion chamber, through an annular space around the central column, into the lower drying chamber, and from the combustion chamber through an outside conduit into the top drying chamber. The volume of these circulating gases is regulated to maintain the temperature in the lower chamber at 450° to 500° F., and at 250° to 350° F. in the upper chamber. From the drying chambers, the gases are returned again to the combustion chamber, through the burner, with the dried concentrate and the air required for combustion. This so-called circulation step performs the two important functions, whereby not only is the wet concentrate dried, but the temperature in the combustion chamber is controlled. Without this step, roasting capacities would be very limited, as otherwise it would be very difficult to maintain the temperature within the operating limits.

Gaseous Products.—The final gaseous products of combustion leave the furnace through the exit between the two collecting and desulphurizing hearths, except when a portion of them is diverted through the sulphating chamber. These gases contain about 9 per cent sulphur dioxide, and a dust burden equal to between 30 and 40 per cent of the weight of the concentrates. They pass directly into waste-heat boilers or, if concentrates of low thermal value are being treated, first through a heat exchanger where the secondary combustion air is preheated. At Trail, heat exchangers are unnecessary, and the gases pass directly from the furnace either into two vertical fire-tube boilers per furnace or into a single, vertical, water-tube boiler per furnace. The fire-tube boilers were installed at first, but later installations have been of the water-tube type.

The dust-laden gases enter the boiler at 1500° F. and leave at 500° to 600° F., the outlet temperature depending upon the cleanliness of the tubes. Approximately 200 boiler hp. of steam up to 200-lb. pressure is generated per 100 tons of concentrates burned per day. The boilers have proved very satisfactory in every way, causing practically no loss of operating time on the furnace except a few hours per week for cleaning tubes.

Upon leaving the boilers, the gases pass into two cyclone dust collectors in parallel, where from 85 to 90 per cent of their contained dust is precipitated. This dust, which is equal to from 30 to 40 per cent of the weight of the feed to the furnace, contains 0.7 per cent sulphide sulphur and 3.5 per cent sulphate sulphur. It is discharged from the cyclones through a rotary valve, or air seal, directly into the calcine conveyors, where, along with the product discharged from the hearths, it is conveyed to the leaching plant for the next treatment step. In the early stages of the development of the process, the cyclone and cyclone-fan installations gave considerable trouble, but the difficulties have been overcome and the cyclone equipment has more than justified its installation, particularly in regard to over-all dust-catching efficiencies, and from the viewpoints of operating and original capital cost.

The gases upon leaving the cyclone fans are at 400° F. and have a dust burden equal to approximately 4 per cent of the weight of the original feed. From the fans they flow through an unlined steel balloon flue to a Cottrell electrical precipitator, where 95 per cent of this dust is removed. This results in an over-all dust-catching efficiency of 99.5 per cent, so that the gases entering the contact-acid plant are practically free of dust. The dust caught in the Cottrell, averaging 4 tons per 100 tons of concentrates treated, contains 0.3 per cent sulphide sulphur and 7.5 per cent sulphate sulphur. This is withdrawn from the Cottrell hoppers and is conveyed by means of a vacuum conveying system to a screw conveyor feeding the acid Pachucas. All of the products from the roast are leached directly without further roasting treatment.

Leaching-plant Feed.—The final product from the roasting plant, which is called the "leaching-plant feed," is a mixture of hearth product, cyclone dust and Cottrell precipitator dust. These various products have the average analyses shown in Table 1.

The zinc solubility on the leaching-plant feed is appreciably higher now than when the calcine was produced by the multiple-hearth roasting method, because in the suspension type of roaster, the harmful period (the ferritization period) of contact between the iron oxide and zinc oxide particles is relatively short as compared to that in the multiple-hearth roaster. On some of the particles, such as those precipitated in the cyclones and Cottrell, contact under ferritization conditions is possibly not made at all. This condition, of course, has a more beneficial effect upon that portion

TABLE 1.—*Analyses of Products*

Product	Analysis, Per Cent					Zinc Solubility, Per Cent
	Pb	Zn	Fe	Total S	Sulphate S	
Hearth product	2.3	60.1	13.7	0.8	0.5	86.7
Cyclone dust	5.3	54.3	11.5	4.0	3.0	88.5
Cottrell dust	9.8	42.2	10.2	7.8	7.5	90.0
Leaching-plant feed	3.7	57.3	12.8	2.3	1.7	87.5

of the concentrate in which the zinc and iron minerals are separately crystallized, and would not apply as well to a concentrate composed entirely of marmatite or other isomorphously crystallized iron and zinc mineral. With such a concentrate the iron would form ferrites in either system of roasting, although the ultimate zinc solubility probably would be higher from a suspension roaster, because of the sulphating action on the dust particles and their very brief period under ferritization conditions.

The Trail zinc concentrate is composed chiefly of marmatite, with a small percentage of free pyrrhotite. The ferritization ratio, or units of zinc combined with units of iron, was 0.522 when these concentrates were roasted in the multiple-hearth furnaces, as compared to 0.46 from the present system of roasting. On other types of concentrates, in which a greater proportion of the iron and zinc minerals were separately crystallized, the difference in the ferritization ratios would be still more in favor of the suspension type of roaster.

Dust Collection.—Paradoxical as it may seem, the collection and handling of the large dust burden is accomplished more efficiently and with less difficulty than when roasting in the multiple-hearth furnaces. Then the dust burden was about 15 per cent of the total feed, divided between 7 per cent flue dust and 8 per cent Cottrell dust, all of which required reroasting. Now, although the dust burden is about 40 per cent of the feed, it can easily be collected mechanically in cyclones, which can be placed at the most convenient point to discharge their product directly into the finished-product conveyor. The small amount of Cottrell precipitator dust, averaging about 4 per cent of the total feed, is also finished product, and is air-conveyed directly to the leaching-plant acid Pachucas. This system of dust collection has effectively solved what originally appeared to be an almost insurmountable dust problem, and is particularly applicable because of the small volumes of low-temperature gases. Also, as a result of the lower volumes, the old brick flue, of large cross section, is now replaced by a relatively small unlined steel balloon flue, from which the small quantity of dust that collects in it is recovered by the same air-conveying system as the Cottrell dust.

Adaptability of Process.—Although the development of the burning concentrate process has been chiefly in connection with the treatment of zinc concentrates, considerable work on a small-scale furnace has proved that the process is adaptable to the treatment of various other mineral sulphides. This is eminently true in regard to the sulphides of iron, particularly pyrite, with which most of the small-scale work has been performed. Owing to the flexibility of the process, whereby it can be operated at various tonnage rates, and within broad limits of temperature, and to the almost complete control of the degree of desulphurization, pyrite can be roasted to produce almost any type of product desired, ranging from a completely desulphurized and fused, granular cinder, to a smooth and porous product either desulphurized or in a highly sulphated state. The roasting of pyrite on a standard-sized burning concentrate furnace would produce results that should compare most favorably with those obtained from zinc concentrates, including completely autogenous roasting with high tonnage rates per unit, high concentration of SO_2 in the exit gases, and the recovery of over 2 boiler hp. per ton roasted per day. These factors, of course, connote low installation and low operating costs, and these have prevailed since conversion of the multiple-hearth furnaces to the suspension type.

Leaching and Purification Plant

The treatment is divided into two cycles, the acid or extraction section and the neutral or purification section. The flowsheet in Fig. 2 shows these sections in detail. Essentially the plant has two functions, extracting the maximum amount of zinc, and purifying the resulting solution to yield satisfactory current efficiencies in the tank room, together with the requisite degree of purity in the final bar zinc.

The flowsheet shows that the calcine is added to the neutral side, with only sufficient acid to effect about 25 per cent extraction. Recent developments tend towards modification of this practice, and when advisable, up to 30 per cent of the total feed is added directly to the acid side. A reduction in the circulating load of solution and improved settling conditions on the neutral side result from this change. Roaster flue dust and products from the Cottrell plant are now added on the acid side, thereby materially improving settling conditions on the neutral side.

The neutral thickener underflow, containing about 75 per cent of the soluble zinc in the plant feed, is leached in seven acid Pachucas in series. Return acid from the tank rooms is added to the first Pachuca only and is so regulated that the available acid in the first Pachuca does not exceed 5 grams per liter; this gives plus or minus 1.5 grams per liter acid in the last Pachuca. The strength of acid at this point must be controlled to avoid re-solution of impurities, which are precipitated in the neutral side of the plant.

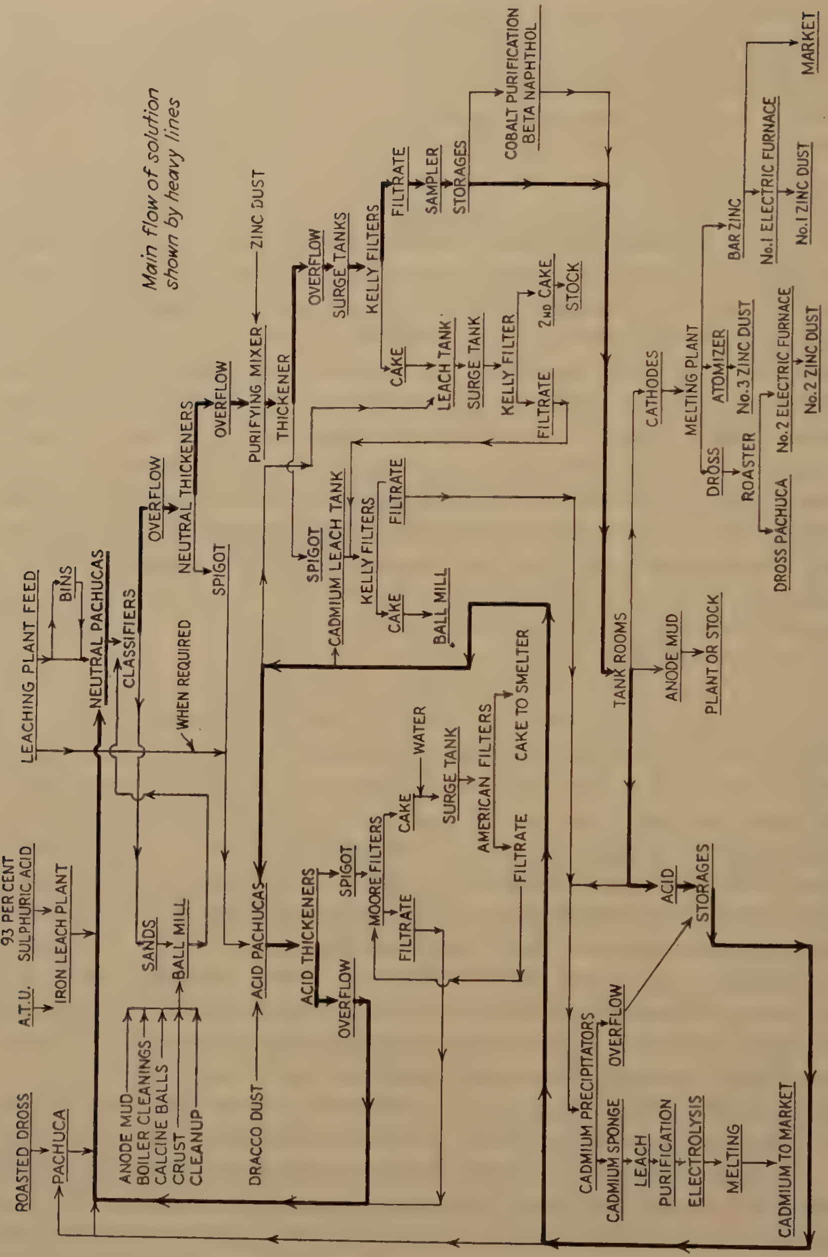


FIG. 2.—FLOW SHEET OF MAIN LEACHING PLANT AT TRAIL.

Acid Pachuca discharge is thickened in eight 50-ft. Dorr thickeners in parallel. The overflow, carrying about 10 grams solids per liter and plus or minus 1.0 grams acid per liter is the feed to the neutral side of the plant. Acid thickener underflow averaging 40 per cent solids is pumped to the filtering and washing section of the plant. There is some further extraction of zinc in the acid thickeners, as evidenced by solution contained in the underflow, which is neutral and carries only about 0.10 grams total iron per liter, all in the ferrous condition. Thickener operation is controlled to ensure neutrality in the underflow. Acid conditions at this point tend towards creating a circulating load of impurities.

Acid thickener underflow at 40 per cent solids is delivered to Moore filters for preliminary washing. The Moore cake is retreated on seven American filters; these are split into two sections of three each with one spare and the sections operate in series. The discharge from the first section of three is pugged with water (Fig. 3).

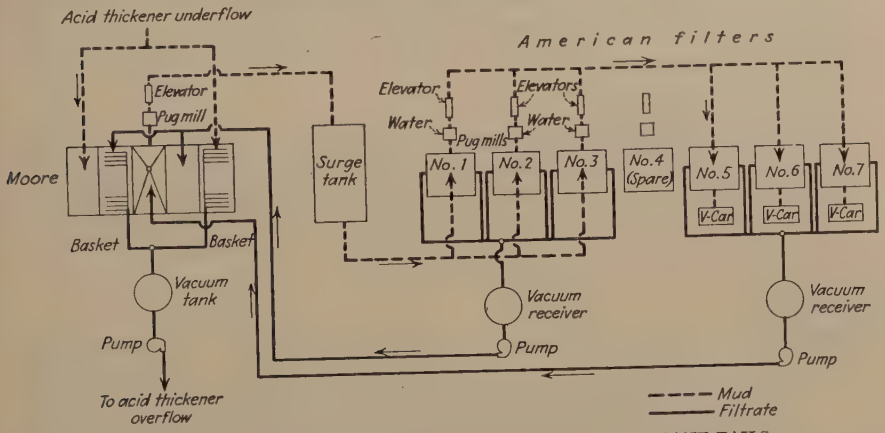


Fig. 3.—Flow sheet of treatment of leaching-plant tails.

The final cake at 30 per cent moisture is discharged to V-cars for delivery to the smelter, where the lead and silver are recovered and the zinc in the form of oxide extracted from the slag is delivered to the oxide leaching plant. A varying percentage of this cake is dried in rotary driers to about 10 per cent moisture before delivery to the smelter. The average assay of this product is as follows for the year 1935: Au, tr.; Ag, 6.0 oz. per ton; Cu, 0.32 per cent; Pb, 11.2; Zn, 20.9; total S, 4.7; sulphate S, 2.6; insoluble, 3.2; Fe, 32.2; Mn, 1.05; CaO, 0.40; Cd, 0.20; acid-soluble Zn, 1.50; water-soluble Zn, 0.92.

Settling and Filtration

The change from roasting in Wedge furnaces to suspension roasting introduced two major problems in the leaching plant. When all roasting was done in Wedge furnaces, settling and filtering equipment was ample for full plant production. After the introduction of suspension roasting, this was not so. Changed roasting conditions had little effect on the acid side of the leaching plant but there was trouble on the neutral side. A study was made of the four products resulting from suspension roasting: (1) the material discharged from the bottom hearth, (2) that caught by the cyclones, (3) balloon flue dust and (4) the recovery from the Cottrell plant. The approximate percentages of these products were 57, 38, 1 and 4, respectively. An empirical laboratory test was developed to make comparisons possible. This test was designed to give comparative results only, but later was found to check very well with plant operation. The test is made by acidifying one liter of neutral electrolyte to 6 grams per liter H_2SO_4 and agitating in a small Pachuca for ½ hr. with 100 grams of the material under investigation. After agitation the pulp is transferred as quickly as possible to a one-liter graduate, where settling time, etc., is determined. The results obtained for the different products were illuminating (Table 2).

TABLE 2.—*Results of Laboratory Test*

Product	Percentage of Total	Volume Settled Solids per 100 Grams Material, In.	Volume Clear Solution, In.
Hearth product	57	2	12
Cyclone catch	38	9	5
Balloon flue dust	1	10½	3½
Cottrell dust	4	13⁹⁄₁₆	⁷⁄₁₆

It was not normal roaster practice to collect balloon flue dust and Cottrell dust daily, these products being added intermittently in amount much in excess of any one day's production. Better distribution of these two products effected a marked improvement in settling conditions. Further investigation showed that when added to the acid side they produced no bad effects, and since they have been transferred to the acid side, no settling trouble has developed with the plant at full production. If necessary, further settling capacity can be obtained by diverting as much as may be necessary of the cyclone dust to the acid side. Laboratory work has shown that reroasting these poor-settling products in a hearth-type roaster or returning them to the hearths of the suspension roaster will cause their settling properties to approach closely those of the

TABLE 3.—*Average Size of Products*

Product	Size Range, Microns	Theoretical Mesh
Hearth product	60 to 1	200 to 10,000
Cyclone catch	20 to 5	700 to 3,000
Cottrell dust	6 to 1	2,000 to 10,000

original hearth product. A microscopic examination showed the average size of these products (Table 3).

These products all settle quite normally in either an acid solution or in plain water. The very poor settling of the Cottrell dust is probably a gas-film adsorption phenomenon.

The effect of suspension roasting on filtration of the plant residues on American filters is illustrated by comparative filtering rates in the plant: In the year 1928, with Wedge roasting, the rate was 915 lb. per sq. ft. of filter area per 24 hr.; for four months in 1931, with suspension roasting, it was 197 lb. per sq. ft. of filter area. This is equivalent to 78.5 per cent decrease in filter production.

Research on improving the filtering rate was undertaken. Pressure filters of the Kelly type gave only 49 lb. per sq. ft. per 24 hr. This type of filter is not adaptable to washing the cake satisfactorily. With ground limerock as filter aid, it was necessary to use about 15 per cent of the dry weight of residue to obtain any material increase in filtering rate. Filter aids such as "Super Cel" were effective only in amounts averaging 20 per cent of the dry cake. Increased temperature improved filtering rates materially but as live steam had to be used too much dilution resulted.

Slacked lime added to the filter feed gave much the best results; 18.5 lb. of lime per ton of cake improved the filtering rate 66.0 per cent. Unfortunately, too much zinc was precipitated to make this method economical. Reroasting of the cyclone and Cottrell dusts doubled the over-all filtering rate. Changing the filtering medium from wool to canvas effected some improvement due to better removal of the very thin cake. Roller scrapers on American filters also effected a marked improvement due to better removal of the cake.

Varying filter speed from 180 to 75 sec. per revolution was not effective, as the cake at the higher speed was too thin to be removed. It was known that after the first filtration, successive filtrations became much easier, owing to replacement of $ZnSO_4$ by water. A small commercial Moore filter was installed, and this indicated that if the first filtration were made on such a filter the existing installation of American filters would be sufficient. Since the present Moore filters were installed in 1934, no trouble had been experienced in handling the plant residues at full production. The filter rate of the American filters since installation of the Moore filters has averaged 310 lb. per sq. ft. per 24 hours.

Purification Section

The acid thickener overflow containing the extracted zinc together with soluble impurities is treated in eight Pachuca tanks, in two series of four tanks each section, the bulk of the calcine being added to the first Pachuca of each section. The analysis of the acid thickener overflow for 1935 is as follows:

Grams per Liter				Milligrams per Liter				
H_2SO_4	Fe''	Fe'''	Al	Cd	Cu	As	SiO_2	Sb
0.9	0.24	1.10	0.169	189	600	18	867	0.7

The excess of zinc oxide brings the solution to a pH of 5.3, at which point iron and aluminum are precipitated as hydroxides. Such impurities as As, Sb, Ge are adsorbed or precipitated with the iron and finally are discarded in the plant rejects.

The neutral Pachuca discharge is distributed to thickeners, the underflow progressing to the acid leaching section. The relatively clear overflow (0.5 grams per liter solids) is purified in batches for copper and cadmium, with zinc dust at plant temperature, which averages 40° C. At Trail temperatures, little cobalt is removed with zinc dust.

Copper and cadmium purification is made in batches in mechanically agitated tanks of 40 water tons[1] capacity. Zinc dust is added in amounts varying from 0.75 to 1.50 grams per liter, the amount depending on the final grade of bar zinc required and the type of zinc dust used.

The removal of cadmium below 3 to 4 mg. per liter, which is necessary for making die-casting grade of zinc, is difficult and requires a great excess of zinc dust when accomplished in one treatment. Better results with less zinc dust can be obtained by purifying in two steps with intermediate filtration. With 10 to 15 mg. per liter left after the first treatment, the second will give 1 mg. per liter, or less.

Plant-scale experiments in adding zinc dust to the intake of a centrifugal pump have been very successful, both for one-stage or two-stage purification. This method is similar to standard cyanide practice and, as in cyanide work, very fine zinc dust is necessary. Electric-furnace dust, mentioned below, is ideal for the purpose. For new construction this method of precipitation would effect substantial savings in plant equipment. Two types of zinc dust are in use:

1. Dust made by atomizing with high-pressure air, the screen analysis of which (Tyler) is as follows:

+20	+48	+100	+150	+200	−200
0.8	8.4	23.6	9.0	7.8	50.4

2. Dust made from melting-room dross in an electric-arc furnace using coke for reduction. This is a very fine product, the average particle size being less than 5 microns. The electric furnace has not yet sufficient capacity for all plant requirements. This dust, with a metallic zinc content averaging 85 per cent, is much more efficient pound for pound than the air-atomized dust.

---

[1] The term "water ton" represents a volume of 32 cu. ft.

When assays are reported in grams per liter, conversion to pounds per water ton entails only multiplying the assay by two. To illustrate, if the assay is 125 grams per liter each water ton of solution will contain 250 lb., very nearly.

For 1935, the analysis of the solution to zinc-dust purification is as follows: solids, 1.04 grams per liter; Cd, 242 mg. per liter; Cu, 24 mg. per liter; Pb, 12 mg. per liter.

Cobalt purification is made on the purified solution with nitroso beta naphthol. Sufficient solution to maintain the cobalt tenor between 3 and 4 mg. per liter is treated daily; the average amount purified daily is about 900 water tons. Nitroso beta nephthol is made in situ from sodium nitrite and beta naphthol dissolved in caustic soda.

The analysis of purified solution fed to the tank room for 1935 is as follows:

GRAMS PER LITER
Zn 127, Fe″ 0.016, Fe‴ 0.003, Mn 0.56, $CaSO_4$ 1.90, $MgSO_4$ 7.0
MILLIGRAMS PER LITER
Cd 4.5, Cl chloride 30, Cl total 113, Al 12, Cu 0.11, Pb tr., As + Sb 0.08, Co 3.7, SiO_2 133, F_2 23
Sp. gr., 1.303.

The mechanical purifying mixers discharge to thickeners; final clarification is made with Kelly filters. The combined solids, thickener underflow and Kelly cake constitute the feed to the cadmium plant.

Impurities in general fall into three classifications: (1) harmless, (2) detrimental, (3) beneficial.

Sodium, potassium and magnesium are examples of harmless impurities. Unless they build up sufficiently to displace zinc in solution, they cause no trouble. Calcium with its low solubility is harmless chemically, but is troublesome mechanically, crystallizing out in pipe lines and launders. Manganese in solution serves no useful purpose and is an added expense in tank-room operation. As the dioxide, it is useful as an oxidizing agent in the leaching plant.

Elements that lower the hydrogen overvoltage of zinc, such as copper, arsenic, antimony, germanium, tellurium and cobalt, cause definite loss of current efficiency, some even when present to only the extent of a small fraction of one part per million. Antimony, germanium and tellurium are outstanding examples. Cadmium up to 150 mg. per liter causes no loss of current efficiency but reduces the grade of zinc. Fluorine is exceedingly objectionable; it has no effect on current efficiency, but causes abnormal cathode aluminum consumption and sticking of the zinc deposit to the cathode. No commercially satisfactory method for the removal of fluorine from solution is available at present.

Cobalt in suitable amounts is valuable in reducing the lead tenor of cathode zinc, and in reducing the corrosion of the lead anode. If present in excessive amounts, it causes serious reduction in current efficiency. Trail experience is that a concentration of 3 to 4 mg. per liter gives lead control with no loss of current efficiency. Generally speaking, the permissible amount of cobalt depends on what other impurities may be present and on the acid concentration used.

Plant Chemical Control

In the early days of electrolytic zinc, plant results were usually erratic, great variations in current efficiency being the order of the day. It was generally recognized that pure zinc sulphate was essential to good current efficiencies. Ideas on what constitutes a pure solution have been subject to great revision in recent years. For instance, a statement 20 years ago that ¼ part per million of some impurity would seriously affect current efficiency would have been treated with at least considerable scepticism. In recent years the analytical chemist's idea of what constitutes a "trace" has been greatly modified; in those days anything less than 0.10 per cent might be reported as trace or nil; now solution assays are regularly reported in parts per million or fractions thereof.

The failure of the Ashcroft process at Cockle Creek, N.S.W., in 1896 has been attributed to the unrecognized presence of cobalt. In more recent times the East St. Louis plant of the Evans-Wallower Co. ran into serious trouble from an unidentified impurity; i.e., germanium[2].

While the effect of nearly all possible impurities is now known, together with their permissible concentrations, it is obviously impossible to control the daily purity of solutions by analytical means only. The determination of most impurities with the degree of accuracy necessary is time consuming, also the quantities involved may be beyond the range of commercial analysis with the time usually available. The zinc electrolytic cell itself is the most sensitive method available for testing solution purity. The laboratory cell when operated under closely controlled laboratory conditions will indicate the presence of abnormal impurities that might take several days to isolate chemically, and frequently the appearance of the deposit will indicate the offending impurity.

Daily control in the leaching plant consists principally in maintaining a set of conditions that previous research and experience has demonstrated will consistently yield a properly purified solution. Maintenance of correct acidity, the necessary amount of iron in solution, and its proper oxidation are the main points. The variations in impurities removable by zinc dust are not great, so the quantity necessary can be regulated by the grade of zinc desired. All necessary chemical determinations are made with sufficient accuracy by plant operators. Twenty-four-hour composite samples, only, are analyzed in the assay office. The control of slowly cumulative impurities, such as chlorine and cobalt, is regulated by assay.

Daily samples of electrolyte are tested in the laboratory for current efficiency, anode corrosion and cathode corrosion. Daily samples of calcine are also checked for settling.

---

[2] *Trans.* Amer. Electrochem. Soc. (1930) **57**, 279.

Current Efficiency.—Two methods are in use for checking current efficiency. The quick method as outlined by F. E. Lee and A. H. W. Busby[3] takes about ¾ hr. and indicates any serious irregularity in the electrolyte. The other method consists in 18-hr. electrolysis in one-liter beakers, the current efficiency being determined against a solution of known purity and current efficiency, all cells being in series. New lead anodes are invariably used, as they are much more sensitive to changes in solution than stabilized plant anodes, and may show a falling off in current efficiency that will not show up in the plant. This provides a safety factor.

Anode Corrosion.—A new lead anode is run for 18 hr. between two cathodes. The anode is cleaned and the loss in weight is determined. It is also carefully examined for corrosion. Any abnormal corrosion, usually on the solution line, is readily detected by eye. These tests are started at 10 grams per liter acid, and finish at plant acidity. It has been proved that under these conditions corrosion will be in evidence in the laboratory when none is taking place in the plant; thus giving information that plant conditions are approaching the critical stage. Chlorine compounds are the only ones definitely destructive to anodes, as far as Trail experience goes.

Cathode Corrosion.—Aluminum strips of definite area are suspended in both laboratory and plant acid electrolytes for 24 hr., at reasonably constant temperature. The loss in weight is calculated to grams per square foot per 24 hr. C.P. acid electrolyte has a rate between 0.3 and 0.35. An increase to, say, 0.40 to 0.45 is definite evidence of the presence of fluorine. This corrosion rate is at least as accurate as analysis in determining the presence of fluorine, especially in very low concentrations. The corrosion rate for solutions saturated with fluorine will average plus or minus 6.0 grams per sq. ft. per 24 hours.

Settling Rates.—The method employed has already been outlined.

Customs Ores.—All customs concentrates are thoroughly tested in the laboratory before acceptance. They are roasted, leached, the solution purified and the current efficiency determined. The acid solution is analyzed for the usual impurities. Spectroscopic examination is also made to detect such impurities as germanium, tin, etc. Laboratory technique has been developed to simulate closely plant conditions.

Leaching-plant Equipment

The total volume of solution is plus or minus 15,000 water tons; the daily production of finished electrolyte for full production averages 5000 water tons.

---

[3] *Trans.* Electrochem. Soc. (1931) **60**, 197.

Acid Side, Sulphide Leaching Plant.—On the acid side the principal items of equipment are as follows:

Pachuca agitators: seven in series. Same construction as on the neutral side (q.v.). Tops covered and vented to reduce fog.

Thickeners: 8 thickeners, 50-ft. diameter by 12-ft. stave. Capacity, each 530 water tons. Area, each 1960 sq. ft. Total area 15,680 sq. ft. Construction: tank, stem and arms, Douglas fir; rakes, maple; bolts, copper. Speed, 1 revolution in 8 min. Spigot handled by diaphragm pumps. Density controlled by hydrometer readings.

Moore filters: five concrete tanks, 10 by 24 by 15 ft.; two baskets of 29 leaves, each 8 by 6 ft.; 5800 sq. ft. of filtering area. Filtering medium, 12-oz. canvas on cocoa mat backing. Life of canvas, 40 days. Frames, 1-in. heavy-wall copper tubing, with bronze fittings.

American filters: seven filters, each six-disk, 8-ft. 6-in. diameter, 10 leaves per disk. Canvas area each filter, 600 sq. ft. Total 4200 sq. ft. Staybrite steel tanks. Hard lead plate valves with Bakelite wearing faces. Wooden roller cake discharge. Speed, 1 revolution in 2 min., 9 sec. Filter medium, 12-oz. canvas on cocoa matting. Filter frames and central drum of bronze.

Vacuum pump installation: Ingersoll-Rand pumps, six of 2000-cu. ft. per min. displacement, two of 2500 cu. ft. per min. displacement. All driven by 75-hp., 900-r.p.m. motors through Lennox or Tex-rope drives.

Neutral Side, Sulphide Leaching Plant.—On the neutral side the following equipment is used:

Pachucas: 12 Pachuca agitators, each 10 ft. in diameter with 30-ft. staves and 10-in. wooden central column. At present eight are in use operating in two series of four each.

Classifiers: three Dorr Duplex classifiers. Wooden tanks and iron rakes. Rakes, 16 ft. long, 23 in. wide. Speed, eight strokes per minute.

Thickeners: 17 neutral thickeners. Total area 21,130 sq. ft. Total capacity 5410 water tons. Size, etc., shown in Table 4. Tanks and stems, Douglas fir. Arms and rakes, steel. Bottoms are built up to arms with sand. Two of the 50-ft. thickeners have the sand bottom surfaced with 2 in. of gunite, a distinct improvement when cleaning out. The underflows of five thickeners are handled through diaphragm pumps,

TABLE 4.—*Thickener Data*

Number of Thickeners	Diameter, Ft.	Stave, Ft.	Rake Speed, Minutes per Revolution	Capacity of Each, Water Tons	Area of Each, Sq. Ft.
5	32	12	4.5	200	800
9	40	12	4.5	280	1,250
1	50	12	8.0	530	1,960
2	50	15	8.0	680	1,960

the remainder by hoses discharging to a central sump. Density is controlled by hydrometer readings.

Purifying mixers: 16 purifying mixers, each 10-ft. diameter by 18-ft. stave. Capacity, 38.5 water tons each. Agitated by wooden impeller on 8 by 8-in. wooden stem. Overhead drive, stem supported by bronze step bearing. Speed, 40 r.p.m. Discharge through 6-in. valves to common 8-in. manifold.

Kelly filters: 14 filters, five 4 by 10 ft., 450 sq. ft. filtering area; nine 5 by 14 ft., 800 sq. ft. filtering area. Steel construction with 10 leaves to each filter. Leaves made up from iron pipe. Filtering medium, canvas backed by cocoa matting. Feed by centrifugal pump from common 8-in. header. Normal pressure, 50 to 60 lb. per sq. in., maximum 80 lb. per sq. inch.

Neutral electrolyte storages: unlined tanks, two 60-ft. diameter by 12-ft. stave, delivering by gravity to tank rooms.

Ball mill: one mill, 6 by 6-ft. manganese-steel liners, using 2¼-in. cast-iron balls. Feed consists of roaster crusts and balls, plant cleanup and manganese dioxide scale when required.

Pumps: See page 737.

ELECTROLYTIC DEPARTMENT

The installed electrical equipment has a capacity of 54,550 kw., made up as follows:

13 double motor-generator sets,	each 4000 amp. @ 125 volts	500 kw.
10 rotary converters,	each 4500 amp. @ 550 volts	2475 kw.
3 mercury arc rectifiers,	9000 to 10,000 amp. @ 560 volts	5600 kw.

The average current density is 40 amp. per sq. foot.

Electrical units consist of 36 cells arranged in four cascades of nine cells each. Four units in series, totaling 144 cells, make one group. Two rotary converters or one mercury-arc rectifier supplies the power for one group. This gives a power from 9000 to 10,000 amp. and 550 to 560 volts on the bus line. Cells are cast in pairs with a common central wall, so that a unit consists of two rows of double cells. There are four spare units for the mercury-arc and rotary-converter groups, so arranged that any unit in these groups can be cut out for cleaning and repairs. Cells are connected electrically in series, the electrodes in each tank being in parallel. All units are supplied with crane equipment to facilitate cell handling, cleaning and repairs.

Cell Construction

Until 1932 all electrolytic cells were of concrete construction with sulphur-sand lining. This type of cell is reasonably satisfactory but is high in maintenance cost. Rubber-lined experimental cells proved so satisfactory that 55 per cent of the present tanks are concrete with rubber lining vulcanized in situ. The outside of these tanks is protected with either 3-lb. lead sheet or rubber.

The remaining sulphur-sand lined tanks are now being replaced by "Prodorite" tanks, which promise to have a very long life. The Prodorite tanks are cast in one piece with special equipment designed for this purpose.

While Prodorite has been used in Europe for some years, for acidproof tile and sewer pipe, etc., its development for large castings such as electrolytic tanks was pioneered at Trail. Briefly, the plant consists of a stone heater, Prodorite pitch-melting pot, a mixing box and a steel tank mold. The composition of tanks as cast at present is: Prodorite pitch, 7.7 per cent; asphalt, 220° F. melting point, 2.6 per cent; quartz flour, 18.0 per cent; quartz sand, 31.7 per cent; quartz pea gravel, 40.0 per cent. Reinforcing wire required, 180 sq. feet.

The first tanks cast were made without asphalt or reinforcing wire. There was a tendency towards cracking which entailed patching to ensure a waterproof tank. Experiments with different percentages of asphalt resulted in developing the mixture now used, which in combination with reinforcing wire produces a thoroughly satisfactory tank. The tank tops are dressed with sulphur sand to ensure a smooth bearing for the bus bars. The present mixture equals concrete under compression and exceeds concrete in tensile strength.

Electrodes

Anodes are of cast, refined lead, ¼ in. thick, with over-all area of 10.9 sq. ft. having a submerged area of 9.2 sq. ft. There are 24 anodes per tank. The life is considerably in excess of three years. The chemical analysis of the lead used is as follows: Ag, 0.0003 per cent; Cu, 0.0005; Sb, 0.0007; As, tr.; Bi, 0.0003; Pb, 99.998. Discarded anodes are melted and the metal is recast. Anodes are integral with the lead-covered bus bar, being welded thereto, thus ensuring constant spacing. The whole assembly can be raised by crane when necessary.

Cathodes are of high-grade aluminum sheet 3⁄32 in. thick, having the following guaranteed analysis: Si, <0.25; Fe, <0.25; As, nil; Sb, nil; Cu, <0.10; Al, 99.5 per cent. The over-all area is 12 sq. ft., of which 9.4 sq. ft. is submerged. There are 23 cathodes per tank, electrically connected to copper bus bars by a pressure contact. Cathode life is in excess of one year at present. Correct spacing of cathodes is ensured by two spacing sticks of hard wood. These are slotted to fit over the lower ends of the anodes. There is also a cathode slot centrally spaced between two anodes. This arrangement (Fig. 4) facilitates setting and ensures perfect spacing at all times.

Wooden strips slotted to fit over the cathode edges are used to facilitate stripping of the deposit. Spacing between anodes is 3 in. center to center.

Cell Operation

Tank cleaning is done on a 10 to 17-week cycle. Cleaning is necessary when precipitated MnO_2 accumulating in the bottom of the cells causes shorting and lowered current efficiency. When necessary some anode cleaning is done with a special scraper while the unit is in operation, which materially increases the length of the cleaning period.

Electrolyte is fed to each cell individually; the overflows are cumulative. Acidity is regulated by hydrometer readings. It is customary to plate out 55 per cent of the zinc per cycle. Cathodes are stripped once in 24 hr. Attempts to extend the plating period to 48 hr. result in a loss of current efficiency of from 2 to 4 per cent. The loss in current efficiency for periods longer than 24 hr. is due principally to the increased roughness of the deposit, which tends towards the formation of "trees." Once treeing starts, points of high current density develop, which ultimately result in shorts and loss of current efficiency. Wide spacing between anode and cathode improves 48-hr. efficiency materially. Plant results here have shown clearly a great improvement for 4-in. spacing over 3-in. spacing for 48-hr. deposition. Cathodes are pulled individually and stripped by hand beside the tanks. The average pull per man-day is about 5 tons.

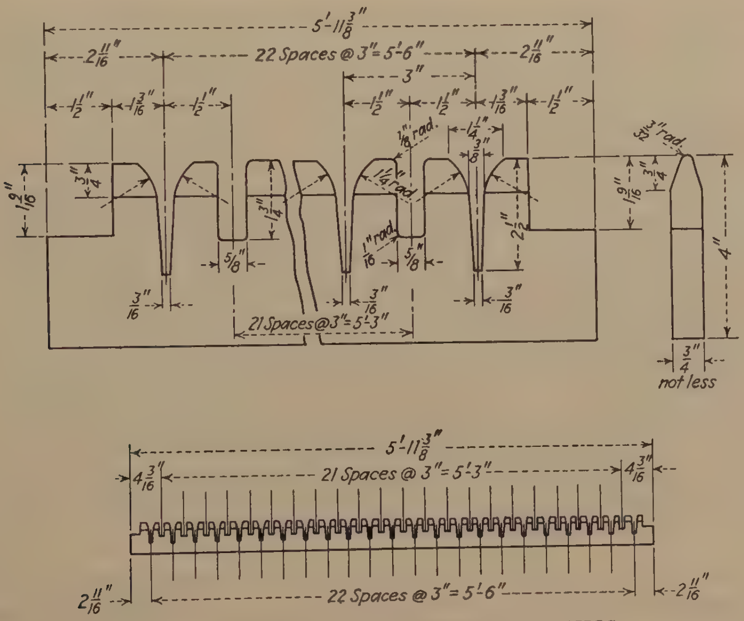


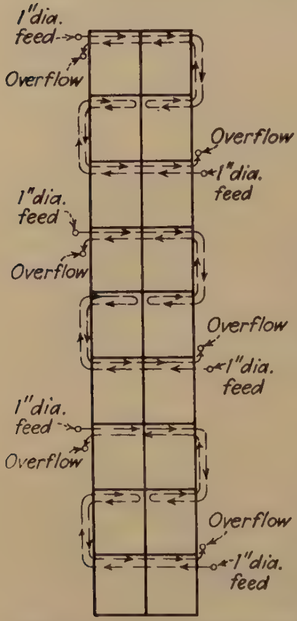
FIG. 4.—SPACER STICK FOR ELECTROLYTIC CELLS.

Glue is added continuously to the feed solution at the rate of 0.20 to 0.30 lb. glue per ton of cathode zinc. Glue tends to reduce the formation of trees and appears to exert a stabilizing effect on solutions slightly below par in purity. The tendency at Trail is towards reduction in the amount of glue used. With the greater purity of electrolyte now normally produced, glue is not so important as it was in the earlier days of electrolytic zinc. At present there are several units that have operated very successfully for several months without any glue.

"Goulac" or "Lignol," which is a by-product of the paper industry, appears entirely satisfactory as a substitute for glue. Goulac is approximately half the price of glue. At present it is being introduced gradually, replacing glue.

Cell Temperatures

Control of cell temperature is an important part of cell-room operation. The effect of impurities on current efficiency is in direct proportion to rise in temperature. The conductivity of the electrolyte decreases with temperature drop. The available water supply and its temperature and cost also affect the cooling problem. For Trail conditions the optimum temperature for cell operation is 35° C., which is maintained with lead cooling coils. A cooling water circuit cools three cells by means of six cooling coils. Each coil is 33 ft. long by 1¼ in. outside diameter, with ⅛-in. wall, giving a cooling area of 65 sq. ft. per cooling unit of three cells. The water used per cooling unit approximates 84 gal. per min., making a total for all tank rooms of 6,500,000 Imperial gal. a day. The temperature difference between inlet and outlet averages 10° C. The range of cooling-water inlet temperature for a year is between 1° and 18° C. In the tank-room section using "oxide" electrolyte, cell temperatures are kept as low as possible. This materially reduces the corrosion of aluminum due to fluorine. Decreased conductivity of the solution is the limiting factor in temperature control in this section. Fig. 5 shows the arrangement of one cooling system.



Sp.

FIG. 5.—PRESENT SCHMEE OF COOLING COILS AND PIPES.

Of the total zinc cathode production, 75 per cent is made from "sulphide" solution and 25 per cent from "oxide." Because of the presence of fluorine in the latter, the two solutions are kept entirely separated. Fluorine causes abnormal corrosion of aluminum cathodes and is responsible for sticking of the zinc deposit to the cathode.

Sticking, and Corrosion of Aluminum Cathodes

From the beginning of operations at the Trail plant in 1916 until 1930, sticking of the zinc deposit to the aluminum cathode was an intermittent phenomenon, varying in intensity, becoming so severe at times that dissolving in acid was the only possible method of removing the zinc. During this period no explanation of the phenomenon was found, despite much research.

When fluorine was added to the electrolyte, sticking ceased being intermittent and became continuous. This suggested that fluorine was probably responsible. Plant results appeared to amply verify this assumption; with reduction of fluorine in the sulphide circuit, sticking gradually diminished and gave no trouble with fluorine at 30 mg. per liter or less.

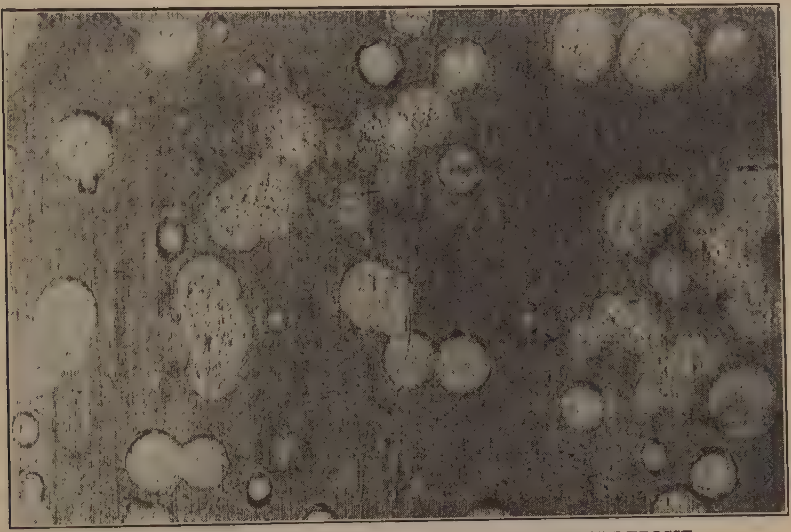


FIG. 6.—CORRODED INNER CATHODE FACE OF ZINC DEPOSIT.

It was noted later that a little spasmodic sticking occurred from time to time, which could not be explained by fluorine. Observations showed that this occurred only where some corrosion of the cathode zinc had taken place. This suggested what now appears to be the true explanation of sticking; namely, that conditions that cause an intensive attack of the aluminum will result in sticking. This hypothesis has been demonstrated on a plant scale, by adjusting cobalt and acidity so that some corrosion of the zinc occurred. This type of corrosion starts at the aluminum cathode side of the deposit, and causes intensified corrosion in spots. Sticking occurs at these corrosion centers.

A photograph of the inner cathode face of a zinc deposit illustrates the type of corrosion mentioned (Fig. 6). None of the holes went entirely through the deposit, but sticking on some of the centers was so intensified that some zinc actually remained in a circle on the aluminum.

Several methods have been developed for control of sticking:

1. Applying a thin slurry of ground anode scale (MnO_2, etc.) in tank-room feed to the aluminum-cathode surface. This method has been used continuously in the plant and has caused surprisingly little loss of current efficiency. The action of this slurry is somewhat obscure, as a similar slurry made from MnO_2 ore not only does not prevent sticking but actually accentuates it.

2. Insulating the cathode in the tank for a short period, averaging 30 sec. to 1 min., before making electrical contact effectively prevents sticking. This method is standard procedure at present in the oxide circuit. Probably a thin film of aluminum sulphate forms on the cathode before electrical contact is made and prevents sticking. The action of aluminum sulphate in preventing corrosion and sticking was discovered at Trail, and is covered by Canadian Patent 333914.

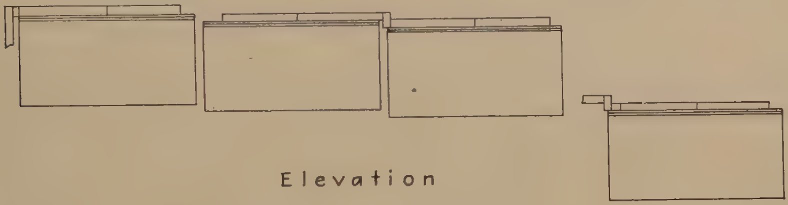
3. Various waxes and gums dissolved in gasoline and applied to the cathode will prevent sticking, but these are difficult to control and constitute a serious fire hazard.

When the oxide plant started operation, the "sulphide" and "oxide" solutions were combined. For five years previous, the consumption of new aluminum averaged 3.2 lb. per ton of cathodes. Fluorine from the oxide practically trebled this figure. Separating these solutions automatically reduced the corrosion by fluorine 75 per cent, after the "sulphide" solution had been freed of fluorine. Fluorine was removed by precipitation with milk of lime. This is not very efficient, but is the only commercial precipitant available. There is some elimination of fluorine by the anodes. Discarded cathodes from the sulphide side are now cut down to 28½ by 22 in. and used on the oxide side instead of new aluminum. The cell size and electrical equipment allow this to be done without unduly raising current density. While the aluminum consumption has not yet definitely reached equilibrium, it appears after a year's operation that the present consumption of new aluminum will not exceed the pre-fluorine period figure of 3.2 lb. per ton of cathodes produced.

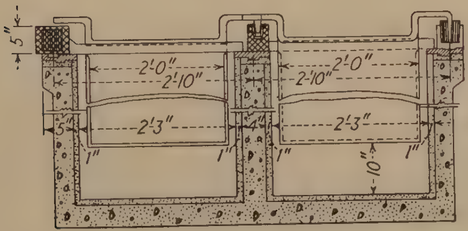
Corrosion of Anodes

Anode life is well over three years. At only one period in the plant's history was serious anode corrosion encountered. During 1931 anode life was reduced to less than six months, because of excessive chlorine in the electrolyte, principally present as perchloric acid, which does not report in the customary method of chlorine determination by precipitation with silver nitrate. There was present over 400 mg. per liter chlorine, only 10 per cent of which was in the form of chloride. During that period of high anode corrosion the lead content of the cathodes was not abnormal.

Oxidation to perchloric acid takes place at the anode. The amount of perchloric acid produced is a function of the chlorine content of the solution and the oxidizing potential of the anode. New anodes produce much more perchloric acid than old ones, therefore many new anodes should not be installed at one time, especially when the chlorine content of the solution is high. Trail experience is that with chlorine as chloride at 30 to 40 mg. per liter the production of perchloric acid is negligible.



Elevation



Cross section

FIG. 7.—ARRANGEMENT OF TANKS AND CROSS SECTION OF A TANK.

Table 5 shows the deportment of chlorine with old and new anodes during electrolysis.

TABLE 5.—*Percentage Distribution of Chlorine after Electrolysis*[a]

	NEW ANODE	ANODE 100 DAYS OLD
Liberated as gas	6.9	18.0
As perchlorate	58.5	30.2
As chloride	34.6	51.8

[a] The head solution before electrolysis contained 128 mg. per liter chlorine as chloride.

All normal production of cathodes is of A grade. The requirements of the die-casting industry call for zinc of lower lead and cadmium content than A grade. The desired grade in lead is obtained by "cropping," cadmium being controlled in the leaching plant.

The lead content of cathode zinc, other conditions being constant, increases slowly with the time the anode has been in use since cleaning. For die-casting grades, cathodes of the requisite lead content are segregated and melted separately. This constitutes the "cropping" operation. The cobalt content of the electrolyte is also of prime importance.

Electrolytes are fed to the tank room by gravity from three storage tanks, each 60 ft. in diameter, two for the "sulphide" solution and one for the "oxide" solution. Spent acid electrolytes from the sulphide and oxide sections are pumped separately to their respective lead-lined storage tanks, which deliver by gravity to the sulphide and oxide leaching plants. The analysis of the electrolyte produced in 1935 is given in Table 6. The over-all current efficiency for the year 1935 was: sulphide, 92.3 per cent; oxide, 90.9 per cent.

TABLE 6.—*Analysis of Electrolyte Produced in* 1935

	Grams per Liter							Milligrams per Liter									
	Sp. Gr.	Zn	Fe''	Fe'''	Mn	$CaSO_4$	$MgSO_4$	Cd	Chloride Cl	Tot. Cl	Al	Cu	Pb	As + Sb	Co	SiO_2	F_2
Sulphide feed.....	1.303	127	0.016	0.003	0.56	1.90	7.0	4.5	30	113	12	0.11	Tr.	0.08	3.7	133	23
Oxide feed.......		120	0.021	0.005	1.10	2.10	2.6	10.0	64	142	124	0.22	0.80	0.19	0.20		570
						H_2SO_4											
Sulphide acid.....		54			0.23	107			24								
Oxide acid.......		51			0.27	108											

CADMIUM PLANT

Cadmium occurs only as an impurity in zinc ores; very few zinc ores are entirely free of it. The usual range for concentrates tributary to Trail is 0.10 to 0.30 per cent Cd. Sullivan zinc concentrates average 0.18 per cent. The main supply for the cadmium plant is from the zinc-dust purification residues of the sulphide and oxide plants. A material amount is also recovered from the Cottrell plants and flues at the lead smelter. Cadmium resembles zinc in forming ferrites during roasting. A substantial recovery of the insoluble cadmium is made at the smelter in the zinc oxide fume, flue and Cottrell products.

In Europe, until recently, cadmium was largely recovered by fractional distillation, which produces a relatively low-grade product. On this continent hydrometallurgical recovery is the rule, the product averaging 99.95 per cent cadmium. There are no recognized limits for impurities in cadmium. Thallium is reported to be particularly objectionable. Trail electrolytic cadmium is further refined by the research department and a grade higher than 99.999 per cent Cd is made. It is spectroscopically pure and is being supplied for spectroscopic standards.

Recovery from Zinc Concentrates

The flow sheet of the cadmium plant at Trail is given in Fig. 8.

Soluble cadmium in zinc calcine goes into solution with zinc, and is recovered together with copper, etc., by precipitation with zinc dust. This zinc-cadmium-copper product is the raw material for cadmium production. Its average analysis is Ag, tr.; Cu, 1.91 per cent; Pb, 3.7; Zn, 69.5; Fe, 0.2; Cd, 8.3; Co, 0.02; In and Tl are present.

This product is given a finished leach with acid zinc electrolyte, taking the zinc and cadmium into solution and leaving the copper and lead in the residue. Leaches are finished to a constant acid concentration of 8 to 10 grams per liter H_2SO_4. The leached residue assays: Zn, 6.5 per cent; Cd, 1.5; Pb, 10.7.

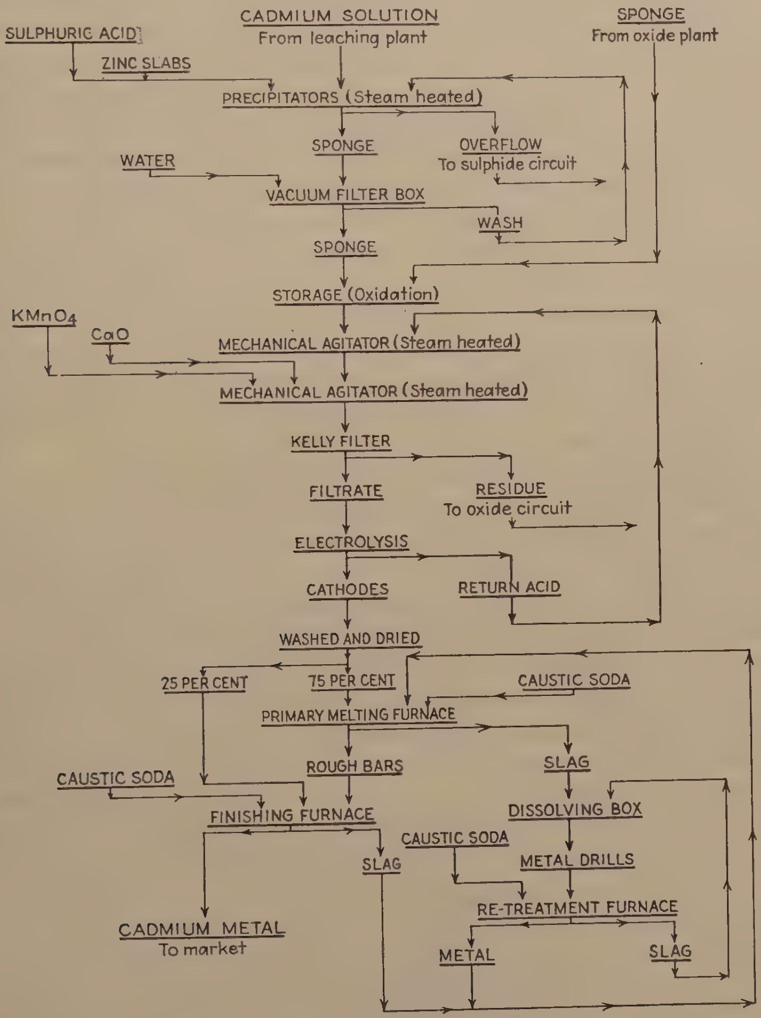


FIG. 8.—FLOW SHEET OF CADMIUM PLANT.

This residue is returned to the acid side of the sulphide plant for further leaching and finally reaches the smelter with the other zinc-plant rejects.

The solution from leaching the primary cadmium cake is as follows: H_2SO_4, 10.5 grams per liter; Fe, 0.97; Mn, 0.87; $CaSO_4$, 2.4; $MgSO_4$, 3.3;

Cd 7.5 grams per liter; Cl, 42 mg. per liter; Cu, 1.5; As + Sb, 1.8; Co, 15 mg. per liter.

The cadmium is precipitated in sponge form on suspended bars of zinc in lead-lined tanks, in which the solution is heated to 70° to 75° C., by steam coils. The sponge produced floats and is recovered largely from the surface of the tanks. After precipitation solution assaying H_2SO_4 1.5 and Cd 0.35 grams per liter is returned to the main leaching plant. When necessary cobalt is removed by the copper-arsenic zinc-dust method.

Free acid greatly improves the precipitating rate and prevents the formation of basic salts and contamination of the sponge. The cadmium sponge is precipitated on bars of zinc in preference to atomized zinc. While the efficiency of the bars is lower, a much higher grade of sponge is produced. Recently experiments with electric-furnace zinc dust have given results comparable to precipitation on bars, and much improved zinc efficiency. The sponge is thoroughly washed with water in vacuum boxes and stored for some weeks to allow some oxidation. Unoxidized sponge is very difficult to dissolve. Sponge assays: Cd, 75.0 per cent; Zn, 5.0 per cent. The oxidized sponge is dissolved in return acid from the cadmium electrolytic cells and after purification forms the feed to the electrolytic cells.

Fortunately cadmium deposition is relatively unaffected by amounts of various impurities that would seriously affect zinc deposition. It is practically impossible to wash all the entrained zinc from the cadmium sponge, so zinc is a cumulative impurity in the electrolytic cycle. Zinc is controlled by preferential precipitation with milk of lime. It is only necessary to maintain the zinc tenor at a point where there is an excess of cadmium over zinc in the spent electrolyte of 10 to 15 grams per liter. Other impurities, such as cobalt, arsenic, antimony, thallium, etc., are removed when necessary by potassium permanganate purification. Analysis of the cadmium electrolyte is given in Table 7.

Table 7.—*Analysis of Cadmium Electrolyte*

	Grams per Liter							Milligrams per Liter		
	Zn	H_2SO_4	Fe	Mn	$CaSO_4$	$MgSO_4$	Cd	Cu	As + Sb	Co
Cell feed..................	31	nil	0.02	0.21	2.2	8.3	177	1.4	0.3	63
Cell discharge............	31	65		0.17	2.2	8.3	104	0.70	0.3	62

Cadmium electrolytic equipment, cells and electrodes are the same as those used for zinc deposition. The current density is 4.00 amp. per sq. ft. Cadmium tends to form "trees," which makes necessary this very low current density. The optimum temperature for electrolysis is 30° C. Cooling is seldom necessary in the summer and during the winter it is frequently necessary to use steam in the cooling coils, to maintain the temperature. Solutions that are too cold produce excessive trees.

Forty-eight-hour deposits are made with a current efficiency of 85 to 90 per cent, trees being removed after 24-hr. deposition. Cathodes are washed with water, rolled in bundles as tightly as possible, dried in an electric drier, melted under caustic soda in a bottom tap pot, and cast in 70-lb. bars. These rough bars are remelted in a separate pot under caustic, and cast in shapes to suit trade requirements. Pencils, balls, anodes, bars and rolled sheets are regularly produced. Melting recovery averages 95 per cent. Of the 1935 production, 67.5 per cent was sold in pencil form. Pencils are ½ in. in diameter and 10 in. long. As pencil casting is both slow and expensive, extrusion has been experimented with, and found quite feasible.

Trees are briquetted in a screw hand press and are melted with the cathodes. Formerly slags were water-leached and the metallics therefrom were dissolved in cadmium acid electrolyte; now cadmium slags are acid-leached in the overflow of the electrolytic units. Analysis of cadmium produced is: Pb, 0.025 per cent; Cu, 0.005; Zn, 0.006; Fe, 0.0004; Cd, 99.964 per cent by difference.

Oxide Leaching Plant

The oxide leaching plant is devoted to the recovery of metallic zinc from the zinc oxide produced by re-treatment of the smelter lead blast-furnace slag. This section started operation in 1930 and has been in continuous operation since then. The development of the process, the difficulties encountered, the impurities found, and their effect, have been covered in some detail in a paper by Hannay and Bryden[4].

The oxide plant differs in two ways from the sulphide plant. First, there is no return from the neutral circuit to the acid side. The amount and nature of the impurities, most of which are collected by the iron precipitation, are so great that any return to the acid circuit would involve building up a cycling load. Second, the final purification is made at elevated temperatures, 70° to 75° C. Some copper is added as sulphate, and much more zinc dust is required, 3 to 5 grams per liter.

The flowsheet of the plant as developed to date is shown in Fig. 9. No major changes in treatment have been made since the original flow sheet was published. Three minor changes have been:

1. Shriver presses have replaced Kelly filters for the filtration of solution from final purification, and have proved entirely satisfactory. Paper with canvas backing is the filtering medium employed.

2. A partial leach of the neutral thickener underflow is now made, which materially reduces the percentage of true acid-soluble zinc. The neutral thickener underflow is treated in mechanical agitators with return

---

[4] *Trans.* Can. Inst. Min. and Met. (1934) **37**, 141.

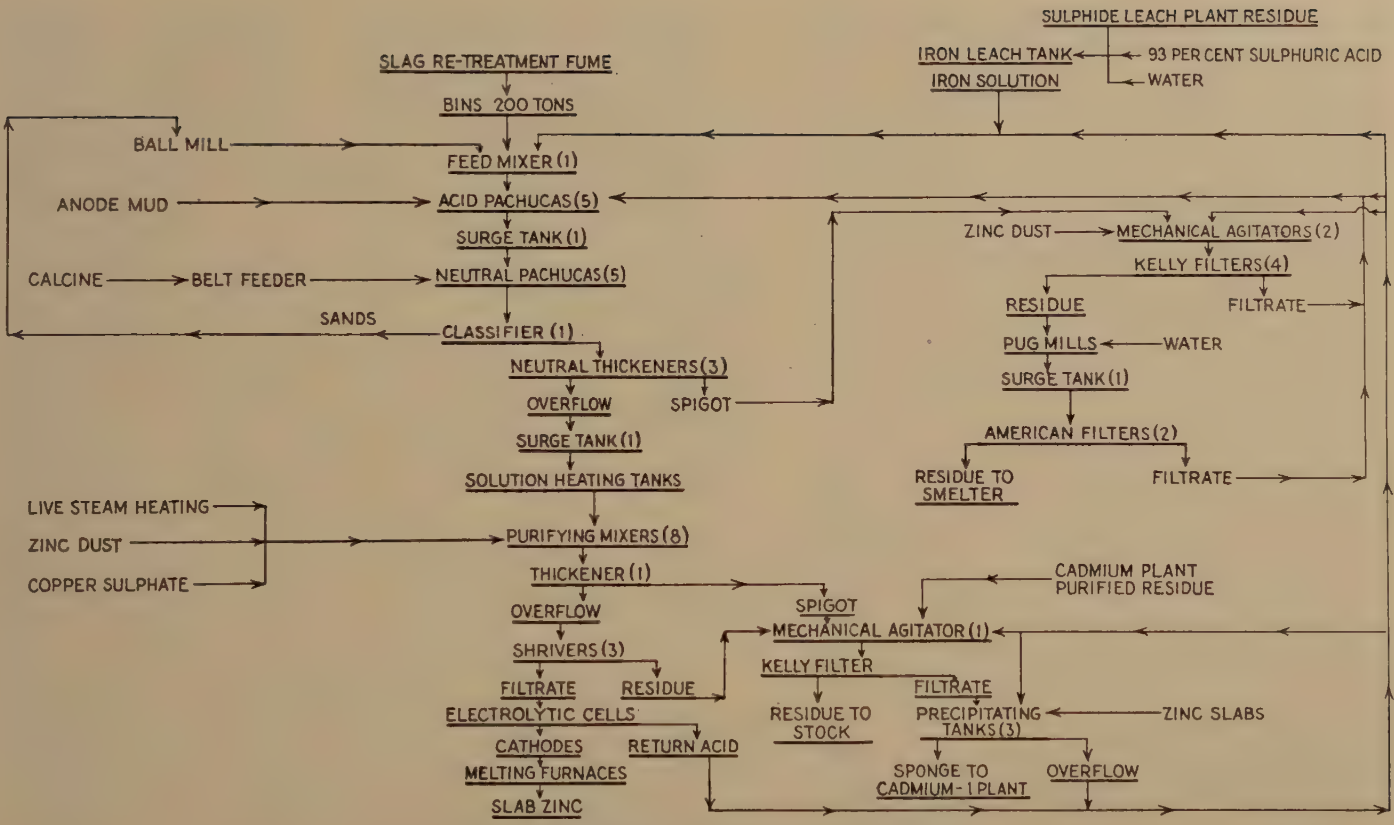


Fig. 9.—Flowsheet of oxide leaching plant.

tank-room acid; the amount of acid used is controlled to ensure neutrality in the finished leach. Slightly more than the theoretical amount of zinc dust is added to preferentially precipitate copper, thereby saving pump and press corrosion. If an excess of acid has been used, it can be neutralized by limerock, or more neutral thickener underflow can be added.

3. The final zinc-dust purification residue is now leached and the cadmium sponge precipitated in the oxide plant, only finished cadmium sponge being sent to the cadmium plant. This ensures keeping practically all the fluorine out of the sulphide circuit. Purification residues from the cadmium electrolytic circuit also are now returned to the oxide plant for the same reason. There is a very marked concentration of fluorine in the cadmium products of the oxide plant, assays ranging from 1.0 to 3.5 per cent fluorine.

The oxide plant uses an average of 27 tons of sulphide calcine daily for neutralization of the acid circuit. Neutralization with oxide fume has been tried from time to time, but owing to considerable variations in the contained impurities and to their appreciable solubility in neutral solutions, fume for neutralization has not been satisfactory. Until recently, calcine was delivered to the oxide plant by cars, which involved much dusting, but a satisfactory method of transfer by air pressure has been developed. The essentials are a pressure storage tank, a pipe line and a receiving bin. The pressure tank is 14 ft. by 4 ft. in diameter;

TABLE 8.—*Assays of Fume, Products and Solutions of Oxide Plant*

	Cu, Per Cent	Pb, Per Cent	Zn, Per Cent	Total S, Per Cent	Sulphate S, Per Cent	SiO_2, Per Cent	Fe, Per Cent	Mn, Per Cent	CaO, Per Cent	Cd, Per Cent	As, Per Cent	Sb, Per Cent
Fume from baghouse........	0.06	9.6	67.7	0.9	0.9	0.4	0.20	0.05	0.2	0.07	0.09	0.09
Fume from flues............	0.09	16.6	57.2	1.4	1.2	2.2	0.80	0.06	0.3	0.07	0.17	0.09
Fume from boilers...........	0.19	16.6	44.4	0.7	0.5	9.1	5.7	0.15	1.7	0.04	0.10	0.09
Plant residue...............	0.24	33.5	9.3			3.3	13.0	0.79	0.7	0.12	0.30	0.31

	Grams per Liter				Milligrams per Liter					
	Solids	H_2SO_4	Fe″	Fe‴	Sb	Cd	Al	Cu	As	SiO_2
Acid Pachuca discharge............	28.1	1.8	0.07	1.90	41	357	482	97	28	84
Neutral thickener overflow..........	0.50	nil	0.01	Tr.	0.60	357	482	33	0.10	84

	Grams per Liter						Milligrams per Liter								
	Zn	Mn	Fe″	Fe‴	$CaSO_4$	$MgSO_4$	Cu	As + Sb	Chloride Cl	Tot. Cl	Pb	Cd	Al	Co	F_2
Purified solution......	120	1.10	0.02	0.005	2.1	2.6	0.22	1.9	64	142	0.80	10	124	0.20	570

capacity 7½ tons. It is filled by gravity from calcine-storage bins. The pipe line consists of 400 ft. of 3-in. pipe, with a rise of 50 ft. The receiving bin is equipped with filter-cloth bags for air release. Air is 367 cu. ft. per min. at 77 lb. pressure. Average time of blow is 25 minutes.

At first, oxide and sulphide electrolytes were combined, but fluorine caused very severe cathode corrosion and "sticking" over the tank rooms. Since October, 1933, the two solutions have been completely separated.

Assays of the fume and the main products and solutions in the oxide plant are given in Table 8.

Oxide Leaching Plant Equipment

The principal items of equipment are as follows:

Acid Side.—Five Pachuca tanks operating in series, connected by 10-in. wood-stave pipe; staves of Douglas fir, 10 ft. in diameter by 30 ft. Bands lead covered. These tanks are covered and vented through the roof. Venting reduces moisture in the building, and a little SO_2 is also present at times.

One Dorr thickener, 50 ft. in diameter by 15 ft.; staves of Douglas fir. Capacity 690 water tons. This tank is used only as a surge tank between the acid and neutral circuits.

Two acid-storage tanks, lead lined; 60 ft. in diameter by 11 ft. 4 in. deep. Capacity 1000 water tons each.

Neutral Side.—Five Pachuca tanks of the same construction as the acid Pachucas, operating in series.

Three 50-ft. Dorr thickeners, operating on the neutral Pachuca discharge. These are of the same size and construction as the acid thickener.

One 50-ft. Dorr thickener, acting as a surge tank between the neutral thickeners and the purifying mixers. Solution from the electric solution heaters is discharged to this tank, which is covered, and vented through the roof.

One 50-ft. Dorr thickener, acting as a surge tank and thickener between the purifying mixers and the Shriver presses.

Seven purifying mixers, 10 ft. in diameter with a capacity of 38 water tons each; 16-ft. staves of Douglas fir. Stem 8 by 8-in. carried on a ball-thrust bearing on top and a bronze step bearing on the bottom. Two impellers of hardwood, 4 ft. long. Drive by 7½ back gear motor through a Tex-rope drive.

One purifying mixer, 15-ft. diameter by 15 ft. 6-in. stave. Construction similar to the 10-ft. mixers.

Five Kelly filters, 5 ft. in diameter by 14 ft. long. Filtering area, 800 sq. ft. each. Filtering medium F-16 canvas backed by cocoa matting. Filter frames, etc., are of steel. The shells are lead lined.

Three Shriver presses, each with 39 plates and 40 frames. Filtering area of each press is 890 sq. ft. Filtering medium is 30-lb. creped Kraft paper backed by 4-oz. duck. Standard hydraulic closing device. Operating pressure 5 to 50 lb. per square foot.

Two wooden cooling towers, each 26 by 18 ft. and 23 ft. high. Solution is delivered by a pump through sprays over the top of the tower, and is collected in a lead pan at the bottom. A fan close to the bottom of each tower delivers 8000 cu. ft. of air per min. Average cooling is about 10° C. These towers operate between the leaching plant and the tank room.

One neutral electrolyte storage, diameter 60 ft. by 11 ft. 4 in. Capacity 1000 water tons. Wooden construction.

One feed bin, laminated wood construction. Capacity 6272 cu. ft., or 150 tons of fume. Lined with No. 28 galvanized sheet over ⅛-in. asbestos.

One feed bin, steel construction, 14 ft. in diameter by 20 ft. deep, capacity 75 tons of fume. Part of the fume is too hot as received to handle in wooden bins.

The total volume of solution averages 8500 water tons with a daily production of 1500 tons of finished electrolyte.

MELTING

Five reverberatory furnaces, hand-fired with coal, are used for melting. Four of the furnaces melt cathodes, the fifth is used for remelting skimmings, etc. Some details of these furnaces are given in Table 9.

TABLE 9.—*Details of Melting Furnaces*

No.	Grate Area, Sq. Ft.	Inside		Depth of Bath	Height of Roof	Capacity, Tons per 24 Hr.	Coal Consumption, Tons per Day
		Length	Width				
1	88.4	20′4″	15′0″	3′6″	6′7″	125	10
2	88.5	20′4″	15′0″	2′6″	5′8″	100	8
3	88.5	20′4″	15′0″	2′6″	5′8″	100	8
4	88.5	20′4″	15′0″	2′6″	5′8″	100	8
5	22.0	20′4″	9′0″			25	3

The temperature of the bath is 900° F. Flue temperature is 1500° F. Direct recovery of cathodes to bar zinc is 95.5 per cent.

Charging and Drossing

Cathodes are received directly from the tank room in cars and after weighing are charged through water-cooled charge doors in the roof of each furnace. Usually there are four charges per furnace day. No charging is done on the 11–7 shift till after drossing has been completed. Dross is rabbled in the furnace with ammonium chloride, removed, and re-treated with some additional ammonium chloride in drossing drums, oil-fired when necessary. The metallic zinc from the drums is returned to the furnace. Dross is delivered to the roasting department for chlorine elimination. Dechlorinated dross is either delivered to the leaching plant or reduced in an electric furnace to zinc dust.

Casting

Each furnace has three rows of mold racks. Each row of molds is filled from a ladle traveling on a "crawl." The ladle dips directly either from the furnace well for A grade or from the "Prime West" conditioning pots. The capacity of the ladle is 300 lb. The ladle fills five molds, each bar weighing ±56 lb. Grade A and Prime Western bars are of equal weight, but are cast in molds slightly different in shape. The grade of zinc and the Tadanac trademark are cast on the bottom of each bar. Three grades of zinc are regularly produced:

"A" grade, which consists of directly melted cathodes.

Prime Western grade, which is made up to trade requirements in lead in special oil-fired cast-iron pots. Zinc is transferred from the melting furnaces to these pots, the desired amount of lead is added and mixed by compressed air and the metal is cast.

Die-casting grade consists of specially selected cathodes of the desired grade, melted separately.

All bars are skimmed as cast to make a clean salable bar, and the skimmings, spillage, etc., are remelted in the scrap furnace.

Special grades of Prime Western are from time to time required. These vary principally in their lead and cadmium contents.

The average analysis of the bar zinc produced in 1935 is as follows:

	Pb. Per Cent	Cd, Per Cent	Fe, Per Cent	Cu, Per Cent	Zn, Per Cent by Difference
"A" grade	0.024	0.005	0.0017	0.0010	99.9683
Prime Western	0.78	0.010	0.0220	0.0010	99.1870
Die casting	0.0035	0.002	0.00070	0.008	99.9930

The Trollhättan Electrothermic Zinc Process

By W. S. Landis,* Member A.I.M.E.

(New York Meeting, February, 1936)

In brief, this is the story of an attempt to Americanize a process originally developed in Europe. The story will be recited in two sections, the first dealing with the process as developed by the European engineers; the second containing the improvements and modifications of American origin, together with some details of the operating results of the unit as finally assembled. Developments in other directions in this same field have not, up to the present, pointed out an economic future for the process, therefore our record here is largely a report of development progress. Whether some particularly favorable location will be found at some future time for a commercial installation cannot as yet be foretold. The project is now at a standstill.

The peculiar tools of the electrometallurgist should be of great interest to the zinc smelter. The low thermal efficiency of the zinc retort, its comparatively small-scale unit and its intermittent cycle as it stood in 1925, should make this art a particularly fertile field for the electric furnace. Yet in spite of years of work recorded in volumes of literature, and an expenditure of large sums of money, there is not a single electrothermic zinc smelter operating anywhere in the world. In this industry the electric furnace plays only a secondary part today.

Historical

The first serious proposal to use the electric furnace for the smelting of zinc ores was made by the Cowles Brothers in 1885, but their experimental work did not advance the art to any extent. The next investigator of this field was Dr. Gustav DeLaval, a Swedish engineer well known to the industrial world through his development of the centrifugal and the steam turbine. The DeLaval cream separator is a familiar household appliance in most parts of the world.

Although Dr. DeLaval commenced his experiments in the field of electric zinc smelting in 1893, it was not until 1898 that he had a practicable furnace, even then operating but intermittently. His work was done at Trollhättan, Sweden. He continued to improve this early fur-

---

Manuscript received at the office of the Institute Dec. 5, 1936.

* Vice President, American Cyanamid Co., New York, N.Y.

nace and by 1902 he could continuously smelt a roasted blende, using coke as a reducing agent and lime as a flux, and the first of a long series of patents was applied for. In 1903 a company was organized to exploit this process and commercial plants were built at Trollhättan, Sweden and at Sarpsborg, Norway. The Swedish plant was by far the larger of the two installations.

By 1909 the Swedish plant was operating nine ore-smelting furnaces, each of 350 hp., and in 1913 this plant had 18 smelting furnaces, each of 500 hp., and during the war four more furnaces were added. All of these early furnaces were single-phase with bottom contact and one movable top electrode. Each furnace was equipped with its own brick-lined condenser and the zinc was recovered partly as liquid metal and partly as powder.

The new furnaces built during the war had much larger hearths and were provided with two top electrodes and no bottom connection. One of the electrodes was merely suspended in the furnace and lowered as it was consumed. The other was called the active electrode, and was used to regulate the power of the furnace, the regulation being by hand control. The old brick-lined condensers were replaced by water-cooled steel condensers and all of the metal was recovered in the form of a powder. In order to convert this powder to liquid form, a rotating electric furnace was developed. Articles that had been published confused this rotary furnace with the centrifugal developments by Dr. DeLaval, and an erroneous impression arose that the process itself actually made use of some centrifugal principle. The rotary furnace was of such slow rotation that no appreciable centrifugal force was generated and such a force played no part in the process carried out in this furnace. An attempt to utilize centrifugal force in a furnace built at Sarpsborg was not particularly successful.

Since the smelting furnace operated at a very high temperature, both lead and zinc were volatilized and the product of the rotary furnace, therefore, was a lead-zinc alloy (assuming lead present in the zinc ores). For this reason an electrically heated liquation furnace was added, permitting a separation of most of the lead and producing the European equivalent of our Prime Western spelter.

In order to meet the growing demands for zinc of high purity, there was subsequently developed an electric redistillation furnace, which volatilized the zinc and left the lead and other impurities behind. Thus the Trollhättan process as developed up to 1925 was an all-electrothermic process involving the use of four different types of electric furnaces on zinc and a fifth for lead refining.

The process was well covered by patents, there being more than one hundred taken out in the various countries of the world, practically all of which will expire before 1940.

The Process

The flowsheet of the process as practiced in Sweden in 1925 and prior to the writer's association with this venture is appended (Fig. 1). The general principles were as follows: The sulphide ores were roasted in a multi-hearth furnace and mixed, so as to make the charge as nearly self-fluxing as possible. The smelting operation was carried out in a closed arc-resistance type of electric furnace. The reaction was essentially one of reduction and volatilization, the gangue of the ore being fluxed to produce a fusible slag. The furnaces were charged from overhead bins, the charge

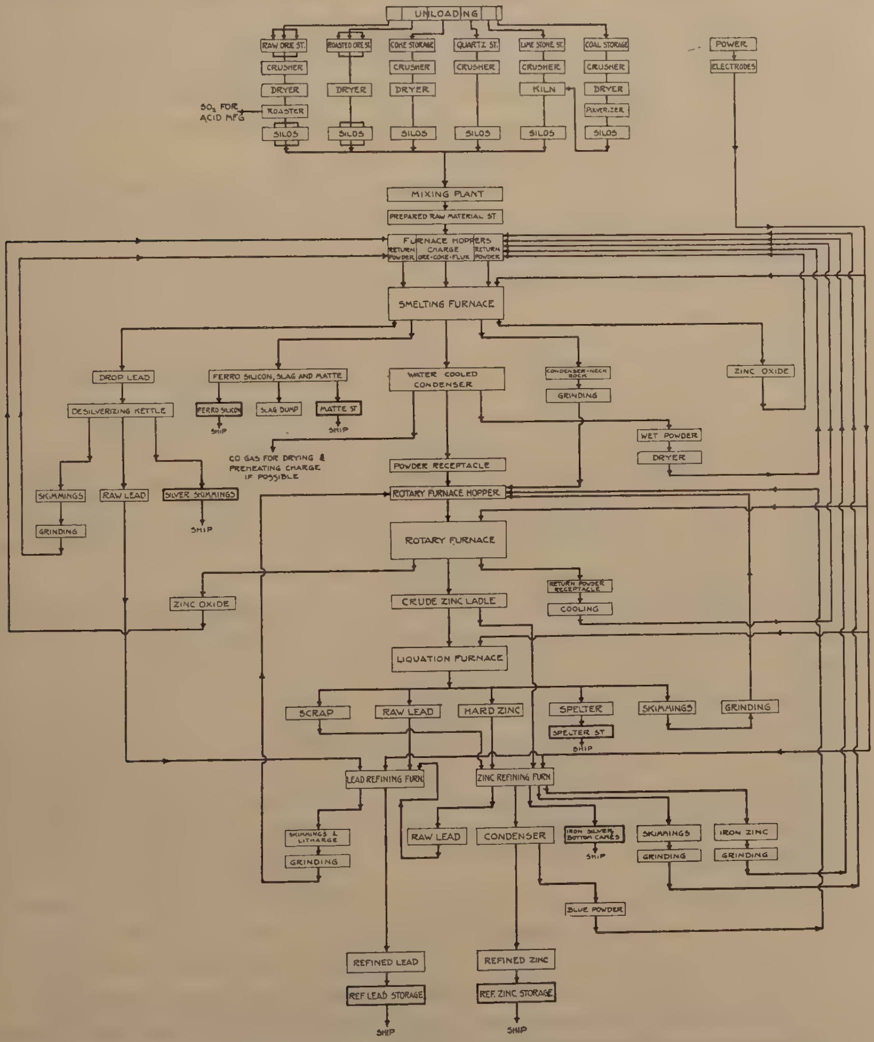


Fig. 1.—Flowsheet of Trollhättan electrothermic zinc process.

consisting of a premixed roasted ore, flux and coke breeze, and if copper was present in the ore sufficient sulfur was left in the charge to produce a low-grade matte. This smelting furnace handled all off-grade slags and mattes, together with any residue of zinc dust not liquefied in the rotary furnace and the various residues from the refining furnaces. There is little likelihood of the freezing up of an electric furnace of this type, therefore the slags produced were calculated more toward a minimum volume than for maximum fusibility. As a matter of fact, during these early years comparatively little progress was made towards a solution of the complicated fluxing problem involved.

The furnace operated in the smelting zone at temperatures above 1400° C., and lead and zinc were volatilized and left the furnace in vapor form mixed with carbon monoxide. This gas stream passed to water-cooled condensers where the metals dropped out in the form of a powder and mechanical screw conveyors were provided for continuously discharging the powder through a suitable seal. The carbon monoxide passed out through a water seal and burned at the exit stack. The character of this flame was an important guide to the furnace operator.

The slag and matte together were tapped from the furnace into slag pots, where the matte settled to the bottom, and was separated by the older system of muscular metallurgy. Gold and silver present in the ores appeared largely in the matte, although some silver was volatilized and recaptured at a later stage in the process.

The zinc-lead powder removed from the condensers was collected in metal containers, which were carried to bins placed above the rotary furnaces. In these electrically heated furnaces, the powder was given a rolling and tumbling at a temperature well above the melting point of zinc. A large part of the powder was rolled into liquid which was tapped from the rotary furnaces at intervals. The unliquefied powder was mechanically discharged through the axis of the furnace and after cooling was carried back to the ore-smelting furnaces, hence the name "return powder."

The molten lead-zinc alloy tapped from the rotary furnace was poured into an open well of an electrically heated liquation furnace operated under close temperature control. Two such furnaces are required to maintain the routine cycle. In this liquation furnace there separates three distinct layers, raw lead on the bottom, hard or iron zinc intermediate, and the equivalent of our Prime Western on top.

The spelter was ladled out and cast into slabs. At less frequent intervals the lead was ladled and cast into slabs or sent to the lead-refining furnace. The iron-zinc at the normal operating temperature of 450° C. is a spongy mass floating on the lead. When a quantity had accumulated, the routine ladling was stopped; the temperature was raised to above 650° C. to liquate as much metal as possible, and the remaining solid was skimmed off with perforated ladles and cast into slabs. This hard zinc carries copper, iron and silver, as well as lead and zinc, and was sent to a refining furnace. A small market was developed for a part of the production. By using two furnaces, one at the low temperature and the other at the high, regular production could be maintained.

Refining was done in a special high-temperature furnace, the hard zinc being subjected either alone or with addition of raw zinc to a redistillation. The refined zinc produced from the hard zinc was never of the highest grade, like that obtained from a refining of the spelter from the liquation furnace.

By redistillation of the liquation-furnace spelter a refined zinc of 99.7 to 99.8 per cent was readily obtainable.

The refining process yielded certain byproducts, such as raw lead, zinc powder, and hard zinc, in addition to the refined spelter that was condensed as liquid. The raw lead was sent to the lead-refining furnaces. The hard zinc was accumulated in the furnace and when it reached a sufficient depth charging was stopped, and the furnace temperature raised to the maximum, after which the hard zinc residue was ladled out. This was cast, crushed and sent back to the ore-smelting furnace. Finally there accumulated in the furnace an "iron-silver bottom cake," which was removed only at long intervals. This cake containing iron, copper and much silver was sold, there being no silver refinery at this plant.

Such was the status when we first became interested in the process. The valuable experience covering a number of years of operation was something to build upon. There were many opportunities for improvement, particularly of equipment. Ores were purchased in the open market, some raw, some roasted, the roasting equipment of small capacity taking care of the raw ores. Many of the ores purchased were cheap because of the penalty carried on the secondary metals, and on a fair zinc market the operation showed a profit. On a declining zinc market the state of development made the operation marginal. We listed the items below that showed the necessity of improvement to put this process on a competitive basis with other zinc-producing methods.

Trouble Analysis

The roasting would have to be more carefully done, since it was necessary to have just the right proportion of sulphur equivalent to the copper present in the heterogeneous ores that could be purchased advantageously. The matte production had been very irregular, sometimes being too low in copper to be merchantable and at other times so high in zinc as to be penalized. Therefore we first set the roaster in regular operation to have a better control of this sulphur content of the charge.

The problem of ore preparation for the electric furnace is always a complex one. In this case it is doubly so because we were dependent upon a very delicate balance in the condenser for the most effective recovery of the zinc and lead. We tried to obtain the maximum of pre-reduction in the roaster in order to keep as much oxygen as possible out of the smelting furnace. Our first efforts were not particularly successful, and later a sintering machine was installed, which very greatly helped in the solution of this problem. We were striving for the lowest state of oxidation of the several minerals present, and we found that a liberal addition of coke dust to the charge on the sintering machine did materially help in eliminating excessive oxygen.

It is very important that water vapor be kept out of the smelting furnace as far as possible. We were forced to use coke breeze as reducing agent, thoroughly dried before charging.

The operations had always been troubled with furnace irregularity. Before the acquisition of the sintering machine they were frequently feeding a furnace charge consisting of a very finely ground concentrate and much coarser coke breeze, various proportions of lump materials such as returned slags, mattes and iron-zinc alloys, and a widely varying quantity of returned zinc powder which had not been liquefied in the rotating furnace. This heterogeneous furnace charge did not feed well down through their furnaces, and these operated most erratically as measured by the power load and the irregular rate of smelting. The charge would hang in the furnace and cause an increase in electrical resistance, necessitating the lowering of the electrode (by hand regulation). The electrode might move some considerable distance before the arch was broken, followed by a drop of fresh charge into an overheated zone, which caused a rapid evolution of vapor and gas, sometimes of such violence as to throw the charge out of the furnace. At the same time this irregular feeding caused an irregular supply of vapor to the condensers. At times these would be overloaded and would discharge zinc vapor into the air through the outlet stack, and sometimes a vacuum would be created in the condensers, drawing in air and causing a more or less violent explosion. In spite of these difficulties, all of which could be traced back to irregular smelting rate of the furnace, this process did produce many thousands of tons of zinc. A larger furnace fed with a burden more uniformly sized was believed to help this situation.

The rotary furnaces that liquefied the powder from the condensers were subject to a great deal of interruption due to electrode breakage. As seen later from the design, these are not the most simple of electric furnaces, and as we first found them they were experiencing more than a usual amount of electrode breakage. This, of course, interrupted their operation, and such interruptions plus the very irregular character of the powder feed to these furnaces, owing to the troubles with the smelting furnace enumerated above, gave a rather poor yield of liquid zinc. We found that over a period of time these furnaces were liquefying only from

¼ to ⅓ of the zinc fed to them and all the rest had to be recirculated to the smelting furnace.

The liquation furnace was a simple operation and gave little or no trouble other than that they were hand-operated and took too much labor, in our opinion. These furnaces were later eliminated altogether and all the raw zinc was sent to the refinery furnaces, which were considerably enlarged.

The redistillation, or refinery, furnaces worked very smoothly and there was little that we could do to improve their operation. It is true that the grade of spelter produced was not as high as we would have liked, as the best we were able to do was 99.85 per cent. This might have been improved by a different system of electric heating of the furnace, but we did not make such changes, believing that another method of treatment of the powder from the smelting furnaces would probably solve all the difficulties. Unfortunately, we were not able to carry out on a large scale our suggested treatment, but the smaller scale experimental work showed great promise. This will be referred to later.

Smelting Furnace

We determined to our own satisfaction that the greatest improvement that we might contribute to this process was a smooth-acting smelting furnace of large capacity, and we debated for a long time as to the proper size for this experimental unit. We all believed that such a unit might be built as large as 10,000 hp., but since we desired to use as much of the auxiliary equipment as we could in the Trollhättan plant, and as there were limitations of power supply, commercial contracts and the like that prevented us from going to this size of operating unit, we compromised on what we termed a 5000-hp. furnace; which actually was officially rated at 4500 kva., three-phase.

The actual problem was not so much in the design of the furnace itself as in the condensing equipment attached to the furnace. We felt certain that we could prepare the furnace charge in such form that it could be fed regularly into the furnace, and that we could provide the furnace with automatic regulators on the electrodes, to keep them active and thus obtain a smooth smelting operation. We were not worried about the minor explosions that were so frequent in the earlier single-phase furnaces. We were concerned, however, with the explosions in the condenser, and we did not wish to build these units so large that if an explosion should occur it would wreck the plant. At any rate, we were forced to compromise on the 5000-hp. furnace, with its more than adequate condensing equipment, as it later proved; and an ingenious device, developed by our metallurgist and installed on the condensers, eliminated all danger of explosion. Accordingly we designed such a furnace with condenser, as illustrated in Fig. 2.

The furnace itself was a rectangular box, thoroughly braced, 21 ft. 4 in. long, 13 ft. wide and of varying height. The roof consisted of half an arch springing from one of the long sides of the furnace and so arranged as to provide an opening opposite the springing line and large enough to carry the vapors into the condenser at considerable velocity. Through the top of the furnace passed three electrodes, 28 in. in diameter. These electrodes were not in one straight line; the center one was pushed forward so as to be nearer the taphole. A hopper overhead contained the furnace charge, which was fed down through pipes through two openings in the roof in front of the two outside electrodes. No feeding was provided between or around the electrodes, nor on the side of the furnace towards the condenser. All openings in the top of the furnace had to be sealed tight, since we intended to carry several millimeters of water pressure. The electrodes, therefore, were provided with packed glands.

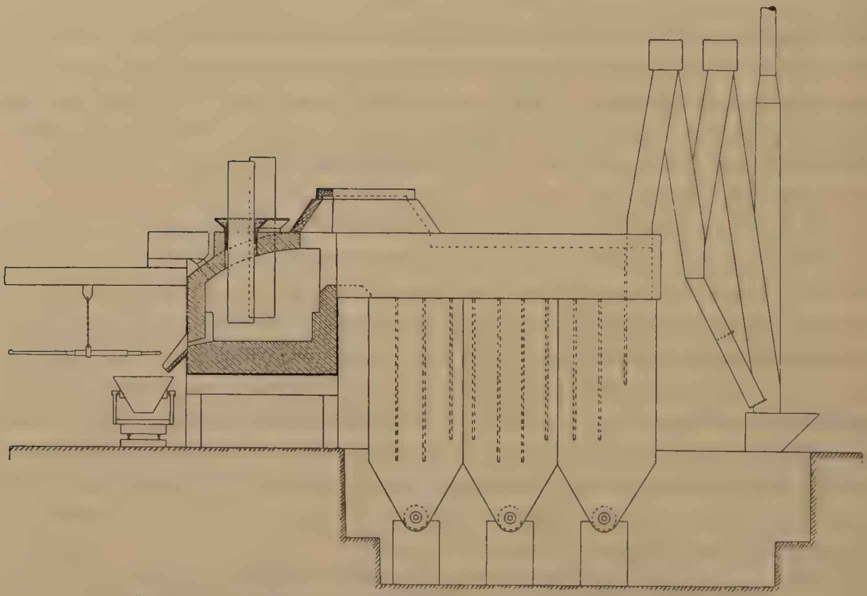


Fig. 2.—Furnace with specially designed condenser.

A single taphole was used for slag and matte, the quantity of matte being too small to even attempt any separation in the furnace.

In the nearly two years of operation this furnace functioned quite satisfactorily. The greatest difficulty we had was the building up of accretions in the furnace neck discharging to the condenser and above the condenser baffle plates. This was a serious problem until we modified and materially enlarged the neck opening and provided suitable cleaning devices that could be operated without unsealing the furnace or condenser. With the changes in these details further changes in the furnace itself were not made during the entire campaign.

For those interested in the electrical equipment, power supply was 25-cycle, three-phase, 11,000 volts. It was stepped down through a bank of three single-phase, 1500-kva. transformers, the low-tension voltage being regulated by means of a primary tap-changing switch to give furnace voltages between 60 and 180 volts in 15 steps, all ratings above 86 volts being of full capacity. External reactance coils were provided to supplement the inherent reactance of the transformers in order to steady the operation, particularly after slagging. The total reactance that could be connected in the circuit was 20 per cent when connected for 180 volts.

The tap-changing switches on the high-tension side were motor operated and were so connected that either a constant current or a constant power input could be maintained. Each electrode was suspended by cable arrangements connected to a motor-driven hoist, and could be lowered by push-button control as it was consumed. It was not believed advisable to control the operation of the furnace by raising or lowering the electrodes on account of the danger of breaking the seal into the furnace around the electrodes.

The entire electrical equipment was supplied by the General Electric Co. of Sweden and worked faultlessly throughout the entire campaign. The transformers were delta connected on the high tension, and star connected on the low-tension side, the neutral being grounded to conducting bars laid in the furnace bottom. This ground connection, however, was found not to be necessary. The entire low-tension bus structure was carefully interlaced right up to the flexibles. Electrodes were purchased from various manufacturers both in the United States and in Europe, and gave excellent service. They were 700 mm. (27.559 in.) in diameter and 2 m. (6.562 ft.) long, and could be joined together by the ordinary screw nipple.

For tapping we adopted the system so highly developed in the carbide industry, the electric tapping needle. A connection is made with one of the electrode circuits connected to an insulated movable graphite electrode enabling us to burn through the taphole. The taphole was plugged with breeze coke.

We recognized the need for a careful preparation on the charge if we were to obtain the maximum of efficiency in our smelting furnace. As stated above, this charge consisted of roasted fine ore. Some of this was jig product; some flotation concentrates. In addition we had to take care of return powder not liquefied in the rotary furnaces, slags, skimmings and other residues. It was extremely difficult to handle such a heterogeneous mixture of products, and the sintering machine was of great help. From a metallurgical standpoint we recognized the necessity for keeping out moisture and reducing the quantity of noncondensible gas discharged from the furnace, and also that it would be advantageous if we could reduce peroxides before feeding them into the furnace.

There is available from such a smelting operation a considerable quantity of carbon monoxide and proposals were made to use this for prereduction of the charge but actually this was not put into practice. Instead a heavy charge of coke was added to the sintering machine, which in part served the same purpose.

The complicated problem of proper fluxing of an electrothermic zinc-smelting operation had to be faced. Previously, experience had greatly varied in the fluxing practice. It was recognized that the electric furnace would melt almost any practicable slag, therefore we were not concerned so much with the question of freezing up of the furnace as we were with making the minimum of slag to conserve electric power. As a matter of fact, the necessary reduction temperatures were so high that the question of low-melting slags never seriously entered into our problem.

Our experience led us to believe that the ideal composition of our slag lay between the following limits: SiO_2, 45 to 55 per cent; CaO + MgO + BaO, 25 to 30; FeO + MnO, 10 to 15; Al_2O_3, etc., 5 to 15 per cent.

A high silica content decreases the tendency of zinc to go into the slag. A high lime content facilitates the separation of matte and slag both through increase of fluidity and decrease of specific gravity. Increase in lime also showed tendency to lower the lead content of the matte. Magnesia is a detriment in that when above 5 per cent it raises the formation temperature and makes the slag too thick.

Apparently the most critical of the constituents of the slag is the iron. A high iron content holds zinc in the slag. On account of the iron content of many of the lower grades of zinc ores, particularly of the complex ores, we had the problem of trying to hold down the iron content of the slag. The solution we worked out for this problem was to reduce this iron and bring it out in the form of a low-grade ferrosilicon. When the furnace was producing ferroalloy we were certain that the slags were clean, frequently running below 1 per cent of zinc oxide. Therefore, we placed very considerable weight upon adding to the high-iron charges sufficient reducing agent to convert the iron oxides of the ore into pig iron or ferrosilicon. This also cleaned more zinc out of the matte, and considerably increased the smoothness of the furnace operation.

Table 1 gives the analyses of some of the zinc ores used at Trollhättan and Table 2 shows the furnace burdens when smelting some of these ores alone without return powder. It is hardly necessary to call attention to the fact that the lime additions should be made in the form of freshly burned quicklime, since we did not want to dilute the gases going to the condenser with carbon dioxide.

TABLE 1.—*Zinc-ore Analyses*

Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Name	Saxberg, Oct. 1925	Ryllshytte	Kalvbäck, Raw	Svardsjo	B.S. No. 1, Raw	B.S. No. 2 or Raib 1	B.S. No. 3, Oct. 26, 1926	Avonmouth	Peru, Aug. 1926	Cartagena	Schwarzwald 10–3–26	Chinese	Potosi	California Trollhättan Lab.	Malines	Ammeberg, Raw
Zn, per cent	36.60	43.50	35/40	36.40	38/39	42.70	42.10	54.80	33.60	44.10	50.50	44.80	53.00	52.80	42.30	39.80
ZnO, per cent	45.60	54.20	44/50	45.40	47/48	53.50	52.40	68.30	41.80	55.00	62.90	55.80	66.00	65.70	52.80	49.60
Pb, per cent	6.95	2.95	3.50	5.10	0.40	5.30	3.50	4.87	11.10	3.40	5.15	9.90	3.95	3.45	10.40	3.60
Cu, per cent	2.70	0.35	0.30	1.30	0.08	0.20	1.05	0.31	1.34	0.21	0.10	1.30		4.88	0.05	0.01
Fe, per cent	12.00	9.88	11.75	10.50	13.34	5.40	8.24	9.50	10.35	14.30	7.46	5.68	11.10	9.00	3.81	2.70
FeO, per cent	15.40	12.70	[b]15.10	13.50	17.15	6.90	10.60	12.20	[b]13.30	18.37	9.60	7.30	14.30	11.50	4.90	3.50
Fe_2O_3, per cent	17.10	14.10		15.00	19.05	7.66	11.84	13.55		20.40	10.65	8.10	15.90	12.80	5.40	3.90
MnO, per cent	0.37	0.77		1.40			1.09	2.15		0.56	0.44	1.00	0.95	0.16	0.15	0.80
CaO, per cent	1.30	3.56	3.50	4.20	0.73	7.38	2.31	1.00	1.30	1.10	1.00	2.30	2.00	0.78	2.50	2.30
MgO, per cent	3.82	4.60	2.60	6.90	tr	4.55	5.16	0.05	0.50	1.17	0.39	0.50	0.43	0.49	1.48	0.60
BaO, per cent	0.14					4.05	0.08	0.08	0.20		2.43			1.76	2.60	
Al_2O_3, per cent	1.70	2.10	2.00	4.00	1.83	2.37	1.16	1.52	2.00	3.83	1.24	1.40	1.52	1.25	2.10	2.60
SiO_2, per cent	7.80	8.58	6.90	11.30	14.06	0.80	10.76	3.40	19.90	11.95	7.91	11.00	3.64	2.43	2.40	23.10
S (total	4.50	4.30		4.00	23.51	5.15	3.40	2.30	3.40	2.07	3.14	3.80	2.74	3.05	5.20	21.70
S (sulphite)	0.30	0.15		0.50		1.20		1.10	0.32	0.39	0.27/0.91	0.20	0.89	0.22	0.50	
Ag (grams per metric ton)	183	40	300/350	100/350 317/200	24		42	256	300/400	90	320/355	240	106	198	450	122
As, per cent					0.16	0.20		0.011						0.10	tr	0.01
Sb, per cent	[a]0.03				0.12	0.02								0.06	0.09	
Bi, per cent	0.00													0.00		
Cd, per cent	0.00			0.041	0.06	0.10		0.129				0.074		0.29	0.22	0.05
Sn, per cent				0.024								0.210				
P, per cent																0.08

[a] As + Sb and Sn. [b] Fe + MnO.

TABLE 2.—*Direct Smelting of Various Ores*
No Return Powder

Type of Ore	Grade	Per Metric Ton Ore				
	Percentage Zn in Ore	Lime, Tons	Silica, Tons	Total Lime and Silica, Tons	Coke, Tons	Smelting Furnace, Kw-hr.
Saxberg, 36 per cent...... Ammeberg, 64 per cent...	40.7	0.025		0.025	0.18	1700
Ammeberg..............	40.0	0.094		0.094	0.20	1750
Saxberg................	42.0	0.163	0.337	0.500	0.25	1975
B.S. No. 3..............	42.1		0.138	0.138	0.20	1780
Saxberg, 40 per cent...... Ryllshytte, 30 per cent... Ammeberg, 30 per cent...	43.6	0.032	0.105	0.137	0.19	1960
California..............	52.8	0.038	0.155	0.193	0.19	1890
All return powder........	55.0					1240

As shown in Fig. 2, the condenser was placed as close to the furnace as construction details permitted. The flue leading to the furnace was a source of considerable trouble because the vapors leaving the furnace, together with fume and dust carried out by the gas stream, tended to condense and bake against the brick lining and gradually fill the passage. This accretion was particularly hard. It was ultimately necessary to enlarge the cross section of the flue and by routine servicing we were able to maintain steady and continuous operation.

The condenser itself was built in three sections, each 7.5 m. (24 6 ft.) high, 2.5 m. wide and 1.5 m. long, giving a total volume of approximately 22 cu. m. (776.8 cu. ft.). The upper part of the condenser and the roof were of brick while the lower portions were constructed of water-jacketed sides with a hopper-shaped bottom. Baffle plates, also of water-cooled construction, served to increase the condenser effect.

In the water-cooled hopper bottom of each of the three sections of the condenser was an extra heavy and powerful screw with a very powerful drive on it. We anticipated that as the smelting operation improved we might have to contend with a considerable quantity of liquid zinc along with the powder and provided heavy equipment for moving a more or less lump product which might have to be torn apart by this conveyor system. These screws collected the powder and carried it outside the condenser through an ingenious sealing arrangement, which prevented the entrance of any air. It took considerable power to push the powder through this seal.

At the far end of the condenser a flue carried up to a damper box, then dropped down to an intermittent collecting hopper, again rising to a damper box and finally dropping down to the floor level, where it passed through a water seal. This water seal was of such depth that we could regulate the back pressure on the furnace and condenser by raising the height of water in the box. From this water seal a pipe led up through and ended above the highest operating floor level on the furnace. The uncondensed carbon monoxide was burned at this outlet within sight of the furnace operator so that he could determine by an inspection of the gases how clear of zinc these gases were. Under normal operation a rather clear blue flame was observable, but at times of irregularity of smelting there usually showed up a zinc flame.

The powder removed by the screws was received in a transport and storage can, one to each condenser section since it was desired to determine the condensing capacity of each section and the nature of the condenser powder. This powder, of course, was somewhat inflammable and when the containers were filled a tight cover was placed over the cans. An overhead crane then removed them to an intermediate storage.

A certain amount of fume and dust separated in the pipe system in the intermediate dust collector and in the water seal. From the former we obtained a small amount of powder, which could go to the rotary furnace. The water seal was cleaned periodically, bringing out a wet mud that had to be dried before it could be sent to the rotary. As a matter of fact, it was so badly oxidized that customarily this dried product was sent back to the smelting furnace.

Apparently our initial design of the condenser was quite satisfactory. The collection of the powder in the three sections for the different campaigns, however, was considerable, as shown in Table 3.

TABLE 3.—*Record of Campaigns*

	Section I	Section II	Section III
60-day campaign on various ores:			
Powder, percentage of total..........	58	28.4	13.6
Total Zn content..................	81.4	85.5	84.4
Metallic Zn content................	66.7	72.8	70.0
17-day campaign on various ores:			
Powder, percentage of total........	32.0	32.4	35.6
Total Zn content..................	82.7	85.2	87.2
Metallic Zn content................	70.5	73.8	74.6

We anticipated a great deal of difficulty with these condensers, having behind us the experience of the many years of operation of the older units

TABLE 4.—*Daily Power Report*

Time	Three-phase Primary		Phase I						Phase II						Phase III					
			Primary				Secondary		Primary				Secondary		Primary				Secondary	
	Kilowatts	Power Factor	Volts	Amperes	Kilowatts	Power Factor	Volts	Amperes	Volts	Amperes	Kilowatts	Power Factor	Volts	Amperes	Volts	Amperes	Kilowatts	Power Factor	Volts	Amperes
7.00	4,200	0.97	10,600	160	1,400	0.88	107	15,000	10,500	165	1,450	0.98	90	16,000	10,600	150	1,400	0.95	130	11,500
8.00	4,200	0.90	10,300	145	1,400	0.85	72	19,000	10,500	150	1,400	0.97	75	18,000	10,500	150	1,400	0.94	90	15,500
9.00	4,300	0.90	10,500	150	1,300	0.96	135	12,500	10,600	140	1,300	0.97	110	13,000	10,600	140	1,400	0.95	115	13,000
10.00	4,300	0.92	10,300	160	1,350	0.94	140	12,500	10,600	160	1,500	0.89	110	13,500	10,400	150	1,400	0.95	98	15,000
11.00	4,400	0.90	10,200	170	1,400	0.93	135	12,000	10,600	165	1,500	0.90	75	17,000	10,500	150	1,400	0.94	85	17,000
12.00	4,400	0.91	10,500	170	1,450	0.90	130	13,000	11,000	160	1,500	0.90	90	16,000	10,500	150	1,400	0.90	80	17,500
13.00	4,400	0.90	10,300	160	1,350	0.93	120	13,500	11,000	160	1,450	0.88	75	17,500	10,600	160	1,400	0.92	72	19,000
14.00	4,300	0.95	10,600	150	1,300	0.90	90	16,000	10,700	140	1,400	0.97	100	15,000	10,600	140	1,350	0.97	110	13,000
15.00	4,200	0.95	10,400	160	1,400	0.95	130	12,000	10,700	150	1,400	0.95	100	15,000	10,500	135	1,300	0.97	120	11,000
16.00	4,200	0.95	10,400	160	1,200	0.96	170	9,000	10,500	130	1,400	0.97	73	11,000	10,500	150	1,400	0.97	110	13,000
17.00	4,000	0.88	10,400	140	1,300	0.80	60	21,000	10,600	150	1,400	0.97	75	18,000	10,500	160	1,400	0.85	75	20,000
18.00	4,200	0.90	10,400	150	1,400	0.85	75	19,000	10,000	150	1,400	0.90	80	17,000	10,500	150	1,400	0.90	80	18,000
19.00	4,200	0.94	10,500	150	1,400	0.90	85	17,000	10,500	140	1,400	0.97	98	15,000	10,500	140	1,350	0.95	120	13,000
20.00	4,200	0.94	10,400	160	1,400	0.95	130	15,000	10,600	140	1,400	0.96	100	14,000	10,600	150	1,500	0.95	95	15,000
21.00	4,200	0.94	10,500	160	1,300	0.96	170	25,000	10,800	140	1,300	0.98	130	10,000	10,500	140	1,400	0.95	100	14,000
22.00	4,000	0.90	10,400	160	1,400	0.95	60	21,000	10,500	130	1,400	0.97	130	11,000	10,600	135	1,300	0.97	120	11,000
23.00	4,200	0.92	10,400	155	1,250	0.95	100	15,000	10,700	155	1,450	0.96	100	14,500	10,500	148	1,350	0.90	80	17,000
24.00	4,200	0.92	10,300	145	1,300	0.90	122	8,200	10,700	170	1,450	0.80	75	18,200	10,500	145	1,350	0.98	78	19,000
1.00	4,200	0.95	10,300	155	1,300	0.93	120	13,000	10,600	165	1,400	0.87	78	17,000	10,400	145	1,400	0.98	170	5,000
2.00	4,000	0.95	10,500	145	1,300	0.86	85	16,000	10,500	140	1,450	0.98	115	12,000	10,500	145	1,400	0.96	142	10,000
3.00	4,000	0.93	10,500	150	1,300	0.80	65	18,000	10,500	138	1,380	0.97	70	17,000	10,500	130	1,300	0.97	135	10,000
4.00	4,000	0.94	10,500	150	1,300	0.90	100	15,000	10,500	140	1,350	0.96	88	15,000	10,500	130	1,250	0.96	170	7,000
5.00	4,200	0.95	10,300	150	1,300	0.90	95	15,000	10,700	155	1,350	0.90	70	19,000	10,400	140	1,350	0.98	140	11,000
6.00	4,000	0.93	10,200	140	1,400	0.80	70	18,000	10,500	180	1,500	0.88	60	20,000	10,500	160	1,400	0.98	110	12,000

in the plant. Irregularity of operation of the smelting furnace would cause air to be sucked into these condensers and cause very violent explosions; or a sudden drop of charge into a heated smelting zone would force a rush of vapor over into the condenser far beyond the capacity to handle, and there would be a violent combustion of zinc vapor at the stack end. We had no knowledge of how smoothly our own furnace would operate, so developed a rather ingenious system for taking care of such irregularity. We installed an extremely sensitive pressure-control apparatus capable of operating on changes of water pressure as low as 5 to 10 mm., and provided an automatic pressure regulator actuating a damper in the water-seal baffle and set to function when the gas pressure in the condenser dropped below or went above the 5 or 10-mm. setting.

We also connected to the condenser a special oil burner that was designed to produce a dry, nonexplosive mixture of nitrogen and carbon dioxide gas. When the pressure dropped below what we considered a dangerous minimum, this oil burner was thrown into operation and flooded the condenser with combustion gases practically free from oxygen. This proved to be an extremely valuable detail, since it enabled us to start up and stop the furnace at will and we could feel as free as possible to experiment with the feeding of the furnace, or shut down for any adjustments, without running the hazards that were so obvious in the older smelting units, where an accidental quick shutdown or starting was always followed by great fear on the part of the management and operators. We never had the slightest difficulty from explosions in our condensers.

We did not operate to produce metallic zinc in the condenser but had prepared, from the knowledge gained in the operation, designs for a new unit, which we believed would permit the handling of both metal and powder. It was never installed.

Table 4 shows a typical daily power report when the furnace was operating at nearly full capacity. It shows how the electrode voltages were varied in order to maintain a practically constant power load.

ROTARY FURNACE

The rotary furnace, Fig. 3, for rolling the metallic powder produced in the condensers was a Swedish development. As we found it, it consisted of a heavy cylindrical shell lined with refractory about 2.5 m. (8.2 ft.) in diameter inside, and approximately 1.5 m. (4.92 ft.) long inside the lining. It rolled on heavy steel tires. About midway between the circumferential lining and the center was arranged a ring of eight carbon electrodes, the ends of which projected through the steel walls of the shell and were insulated therefrom. Originally, graphite sleeves were fitted through the openings in the end walls of the rotating furnace and carbon electrodes, threaded on the ends, screwed into these sleeves and formed the essential heating elements inside the furnace. The eight electrodes were connected in series to collector rings on the hollow trunnions through which the feed was introduced and the unliquated powder removed. Approximately 60 volts was used on the furnace and the current was about 2500 amp. This carbon heating unit was particularly unsatisfactory because of the breakage of the carbon for heating elements, necessitating frequent shutdowns and difficult replacements. We substituted in this built-up heating unit, in which had been used a rather low-resistance carbon, a single continuous high-resistance carbon electrode, of identical size and shape as the previously used built-up construction. The central portion of electrode between the heads was turned down in a lathe to 200 mm. in diameter. By the use of high-resistant carbons without joints we were enabled to cut down the current required and considerably reduced the breakages and consequent interruptions.

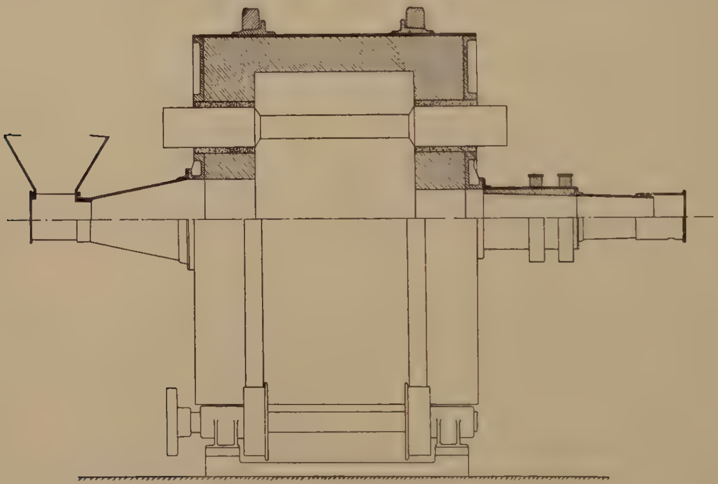


Fig. 3.—Rotary furnace.

The condenser powder, stored in a bin overhead, was fed through a large axial opening in the furnace, by gravity downward and then pushed into the furnace by means of a screw. A similar arrangement on the opposite end discharged the unliquefied powder into a closed container. Unfortunately, this was not an entirely satisfactory arrangement, because the powder came out of the furnace highly heated and, therefore, ignited if exposed to air, and there was considerable burning of the discharged powder. This return powder, as mentioned above, was sent back to the ore-smelting furnace.

A taphole was provided through one of the end walls. By stopping the furnace with this taphole at the lowest position the furnace could be drained of metal content. A tap was made every four hours. About one ton of metal was tapped at a time, the furnaces nominally having a capacity of 6 to 8 tons per day, but frequently exceeding this tonnage if there were no interruptions due to breakage of electrodes. With exceptional qualities of powder, this tonnage would be very greatly exceeded.

Over a long period raw zinc tapped from the rotary averaged about 65 per cent of the ingoing powder, and ingoing powders averaged about 70 per cent zinc in metallic form.

Liquation Furnace

The liquation furnace, Fig. 4, was of rectangular shape, 9 m. long and 1.5 m. wide inside the lining. The roof was horizontal but the bottom sloped so that it was about 1.5 m. deeper at one end than at the other. Above the level of the metal carried in the hearth were arranged three transverse heating electrodes, which extended completely through the side walls and were connected in series. These carbon electrodes were 300 m. in diameter.

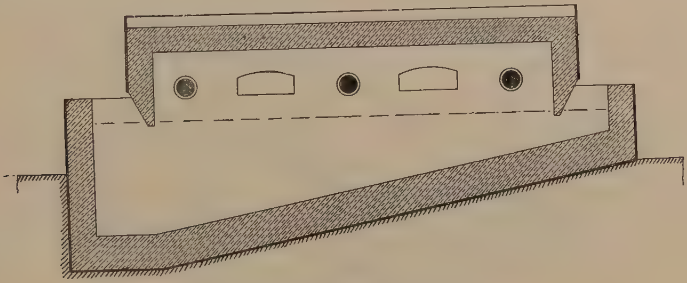


Fig. 4.—Liquation furnace.

The metal from the rotary furnace, called here "raw zinc," carried varying quantities of lead, copper, silver and iron, depending upon the ores smelted. Received from the rotary furnace in ladles, it was poured into a sealed well at the upper end of the hearth and worked its way slowly down to the deeper part of the hearth, separating in the molten bath and lead settling to the bottom. On top of the lead would settle out a hard zinc containing the iron and on top of this would float the G.O.B. metal, as already described.

The zinc produced was a G.O.B., or Prime Western, grade and either was marketed as such or was sent to the refining furnace.

The iron alloy was a spongy hard product carrying both lead and zinc, and some copper and silver, of typical analysis: 90 per cent zinc, 5 per cent lead, 0.25 per cent copper, 5 per cent iron. The product was sent to the refining furnace for the production of high-grade spelter.

The raw lead carried with it 2 to 3 per cent of zinc and had to be softened in a lead-refining furnace.

In our particular development we later omitted the liquation operation and took the metal directly from the rotary to the refining furnace.

REFINING FURNACE

The zinc-refining furnace, Fig. 5, was roughly rectangular in section, of firebrick stayed with structural shapes. It was 3 m. long and 2.5 m. wide and carried at its maximum about one meter depth of metal. One-half meter above the highest metal level was inserted a pair of carbon electrodes 400 mm. in diameter, one from each side of the furnace. An arc was sprung between the abutting ends of these electrodes over the center of the bath. The roof of the furnace, for protection against the intense heat of the arc, was raised nearly 2 m. above the electrode.

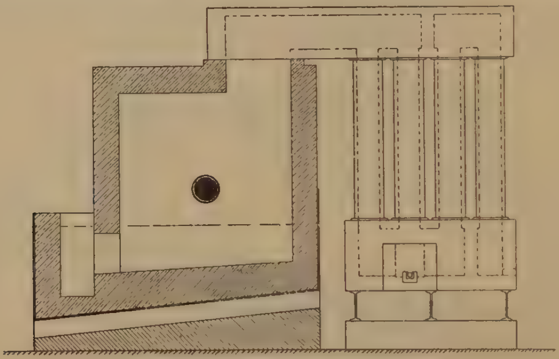


FIG. 5.—REFINING FURNACE.

From an opening in the roof a flue led to a series of vertical oval tubes projecting downward. These tubes were lined with firebrick and free circulation of air was permitted on the outside. They served as condenser for the zinc vapor. An open well received the liquid metal ladled from the liquation furnace, or tapped from the rotaries and the level was maintained nearly constant by replacement of the zinc distilled off by fresh charges. The refined zinc from the condenser was tapped into molds, while the lead, copper and hard zinc carrying iron and silver accumulated in the bottom of the furnace. When these residues had reached a certain depth they were ladled out of the furnace as long as they would flow. There was, however, a very considerable accumulation of iron and hard zinc that was not fusible and ultimately made necessary the cooling down of the furnace so that it could be chipped out. This iron carried a considerable quantity of silver, some examples showing over 2000 grams per ton, or 0.2 per cent. This was silver carried over with a zinc vapor from the smelting furnace which finally collected in this iron alloy in the refining furnace.

It was hoped that ultimately this furnace could be developed to produce a temperature sufficient to melt and tap the iron from the furnace but our work was abandoned before this object was realized.

POWER CONSUMPTION

We carried out four extensive campaigns, three upon miscellaneous varieties of ore and the fourth one on a single Burma ore averaging 57 per cent zinc. On the Burma ore the smelting furnaces consumed 2150 kw-hr. per ton of ore. This was identical with the consumption of the longest campaign made on a miscellaneous lot of ores, but of somewhat lower zinc content.

The rotary furnace showed a consumption on the Burma powder of 325 kw-hr. per ton of original ore smelted. The liquation furnace was not in service during this run.

The refining furnace showed a consumption of 860 kw-hr. per ton of original ore smelted, giving a total of 3335 kw-hr. for all operations and per ton of ore smelted.

At the 89 per cent over-all recovery this would be equivalent to 6550 kw-hr. per metric ton of refined zinc, or practically 1 hp-year.

The electrode consumption average through our campaign on the Burma ore was 4.5 kg. per ton of ore on the smelting furnace, 6.4 kg. on the rotaries and 2.4 kg. on the refining furnace; a total of 13.3 kg. per ton of Burma ore smelted. This naturally included all breakages and losses as well as direct consumption. On the basis of one metric ton of refined spelter, the average consumption was 26.2 kilograms.

METAL RECOVERIES

Metal recoveries are largely dependent upon the character of the ores. Our experience gained in the four long campaigns, on six varieties of ore, led us to conclude that we could expect a zinc recovery in refined spelter of 89 per cent, lead better than 80 per cent, copper 70 per cent and silver over all 70 per cent. The copper and silver recoveries represent not only the products found in the matte but also the additional recoveries in the refining furnace.

If the lead and copper and silver content of the ores are very low, the recoveries will not be so good as when there are larger quantities in the ore. We have gotten even higher lead and copper recoveries than those mentioned above, if the quantity present in the ores is relatively high.

THE BURMA CAMPAIGN

The Burma campaign represented 18 days of operation on a single ore carrying 57 per cent zinc. The total charge for the 18 days to the smelting furnace was as follows: Roasted ore, 648.75 metric tons; returned slags, 26.25; returned powder, 169.80. In addition there was returned for facilitating smelting 22.95 tons of slag that ordinarily would have gone to the dump.

The fluxes used were: lime, 114.60 tons and silica, 155.60 tons. The reducing agent was a coke breeze, 177.67 tons; all metric tons.

The total amounts of metals charged from all of the above sources were: zinc, 482.55 metric tons; lead, 35.82 metric tons; copper, 4.06 metric tons; silver, 200.65 kilograms.

The power consumed on the smelting furnace was 1,398,000 kw-hr., equal to 2150 kw-hr. per metric ton of ore. This is a very high figure, because of the large amount of barren fluxes needed; we wished not to mix ores during this particular campaign. By ore admixture we could have increased the zinc without adding so much barren fluxing material.

The slag made amounted to 437.83 metric tons, of which 403.70 tons went to the dump and 34.13 tons carried sufficient zinc to warrant return to the furnace. This indicates the enormous amount of slag made per ton of ore. The average content of the zinc in the slag sent to the dump was 2.52 per cent.

The matte produced was 32.71 metric tons carrying: zinc, 3.24 metric tons; lead, 0.85 metric tons; copper, 2.82 metric tons; silver, 90 kilograms. This matte carried a penalty because of the high zinc content. The copper recovered as matte was 69.5 per cent of that in the ore charged and the silver recovered in the matte 44.8 per cent. There was produced a total of 6.16 metric tons of ferrosilicon. We should have produced more ferrosilicon and bettered the grade of the matte, and thereby eliminated the penalty.

The condenser powder produced was 511.55 metric tons, practically evenly divided among the three units of the condenser. This powder carried 419 metric tons of zinc, of which 365.20 metric tons was in metallic form. The lead present in the powder amounted to 27.77 metric tons and the silver to 74.89 kilograms.

In addition to the powder produced in the condensers, we obtained 7.83 metric tons from the dust system and 17.43 metric tons (dry basis) from the water seal; there was also picked up 9.6 metric tons in the clean-up operation, or a total of 34.86 tons of other powder.

It was unfortunate that we had to use the rotaries and other equipment in connection with the regular smelting operations in the plant, so that we were not able to completely isolate our data through the remainder of the operations, but emergencies arose whereby additions from the other smelting furnaces complicated our figures.

We had approximately 447 tons of zinc from the Burma ores to go into the rotaries but the rotary charges as listed totaled 515.61, the addition coming from other smelting furnaces. Of this 515.61 tons of condenser powder there was recovered 326.62 tons of raw zinc, 191.86 tons of powder returned to the smelting furnaces. The power consumption was 197,130 kw-hr., which, calculated back to our proportion of the total load on the rotaries and to our ores smelted, amounted to 325 kw-hr. per ton of ore.

The raw zinc from the rotaries ranged in content as follows: lead, 4.8 to 9.3 per cent; copper, 0.05 to 0.22; iron, 0.27 to 1.45. This product was carried directly to the redistillation furnaces and produced a refined zinc carrying: zinc, 99.70 per cent; lead, 0.29; iron, 0.01.

The power consumption calculated back to the original ore was 860 kw-hr. The total power consumption per metric ton of 57 per cent ore on the three furnaces amounted to 3.335 kw-hr., or per ton of zinc recovered, 6550 kilowatt-hours.

The analysis of the other runs would require too much space to be reported here, because mixed ores were used. It may be mentioned, however, that by a proper admixture of ores, fluxes can be materially reduced and much better smelting results obtained.

CONCLUSIONS

We have concluded from this work that one could design and operate an electrothermic smelting plant using smelting furnaces up to 10,000 hp. each. While the rotary is still a small unit, undoubtedly further work would improve its operation. There remains to explore further the elimination of as much oxygen as possible from the ore charge going to the furnace, and a redesigning of the discharge system in the condensers, which should make it possible to produce a considerable portion of the distilled zinc in liquid form. This would involve a slightly different arrangement of condenser, so that part could be run hot and part be water-cooled. There would have to be a redesign of the discharge system, because even the hot condensers would probably pick up some powder. Such improvement seems quite feasible.

The redistillation furnace seems to be a very satisfactory piece of equipment and with more skill in operating the difficulty with the iron cake could undoubtedly be largely eliminated. At present this requires a little more manual labor than should be necessary.

We also carried out on a small scale a modification in which we condensed the vapors in powder form and charged the powder directly to a redistillation furnace, which enabled us to produce refined metal in a single step, but we did not carry this far enough to put it into practice on a large scale, our furnace being only slightly over 100 kw. capacity. There is better than an even chance that this simplification could be developed into an operating unit. This would have the advantage of very greatly simplifying the operation, reducing the attendance and the investment required, and should completely change the complexion of the electrothermic zinc process.

ACKNOWLEDGMENTS

I want to express here appreciation of the work of Mr. E. A. Lof in his contributions to the economics involved in the electrothermic zinc-smelting process, and for his assistance in the preparation of this manu-

script; to the late Mr. E. D. Mathey for the electrical designs involved, and to Mr. F. R. Kemmer, who was metallurgist in charge of the operations. It was through the cooperative efforts of these three engineers that such rapid progress was made in the installation, requiring remarkably few alterations of equipment during the campaigns, and such precise information was acquired under adverse operating conditions. I also must express appreciation to the staff of the Trollhättan Elektrothermiska Aktiebolag for assistance in carrying on the work and permission to use data acquired from the company's records.

DISCUSSION

(*Carle R. Hayward presiding*)

A. ZENTNER,* New York, N. Y. (written discussion).—Mr. Landis and the American Cyanamid Co. are to be congratulated on the most straightforward account that has yet appeared on the electrothermic zinc process. It is the record of an outstanding effort to develop it into large-scale continuous low-cost operation.

I first had occasion to go into the subject in 1911, when the Montana Power Co. urged it upon the Anaconda Copper Mining Co. as a possible large consumer of electric power. The former sent an engineer to the Anaconda Reduction works, where he carried on small-scale work. It devolved upon me to follow this up and to gather all possible information on similar activities elsewhere. After a time it was decided that the process was not promising enough under local conditions to warrant large-scale work on the complex zinc ores available.

Another large company in Montana took up the process, trying it out on high-grade zinc concentrate and spending about $100,000 as I recall it. It is interesting to note that this occurred before electrolytic zinc entered into the affairs of the Anaconda company.

Several years ago the electrothermic zinc plant at Sundlokken, Norway, was offered to clients. The metallurgical results submitted were more or less in line with those presented in this paper.

The power consumption at Trollhättan is given as 6550 kw-hr. per metric ton of refined zinc for ore averaging 57 per cent zinc. The purity of the zinc produced is given as 99.7 to 99.8 per cent. When it is recalled that electrolytic zinc is produced with a power consumption just about one-half of the above and with impurities totaling about one-tenth of the above, it is small wonder the former constituted one-third of the world's total zinc production last year, whereas there was no production from an electrothermic zinc smelter. True, the 6550 kw-hr. includes the formation of some intermediate products, but this factor has not kept any plant operating.

C. H. FULTON,† Rolla, Mo.—You said the power consumption was 6500 kw-hr. per ton of refined zinc. Does that give any credit to the lead production or is all the power consumption charged to the zinc?

W. S. LANDIS.—We figured out the 6500 kw-hr. on the output of refined zinc; that is, throwing all of the power consumption onto the zinc. No power charge was made against lead or matte production, which varied greatly for the miscellaneous ores of this customs smelter.

---

* Consulting Engineer.

† Director, Missouri School of Mines.

E. L. Jorgensen,[*] Irvington, N. J.—What is the composition of this iron-zinc alloy?

W. S. Landis.—The composition of the iron-zinc alloy depends entirely upon the temperature of the unit in which it is produced, inasmuch as the higher the temperature the more zinc can be distilled out of the alloy. A typical iron-zinc alloy taken out of the liquation furnace, which is a low-temperature operation, contained 90 per cent zinc, 5 per cent lead, 0.25 per cent copper and 5 per cent iron. That went back into the original smelting furnace and was handled along with the nonliquefied powder. The content of iron in that alloy went up to 8 and even as high as 10 per cent in the redistillation furnace, where we were operating at much higher temperatures—above 1000° C., whereas we were operating at only 400° C. in the liquation furnace. The average silver runs about 2000 oz. per ton in an iron-zinc alloy from the redistillation furnace.

Member.—What temperatures did you use in the primary volatilization process?

W. S. Landis.—The temperatures were not measured, but from our knowledge of furnaces we judge that the slag was tapped from that furnace at about 1300° C. There is no trouble with freezing up a furnace of this type, for they can always be melted down.

A. J. Phillips,[†] Maurer, N. J.—Why was the powder condensed primarily? Is it a matter of condenser design or a matter of $CO\text{-}CO_2$ equilibrium in the reactions?

W. S. Landis.—I think it is a matter of both. In handling a miscellaneous variety of ores such as we had available, some of the ore was purchased raw and some was purchased roasted. We had available only a limited roasting capacity. Thus we had very incomplete control over the composition of raw materials. Therefore, the $CO\text{-}CO_2$ ratio was largely out of our control.

On account of its influence on the powder condensation, I believe in pretreating the charges—by a partial reduction of the oxide of iron, for example. There is a large amount of oxygen in many of the ores that we used; for most were too high in iron to be usable in the ordinary retort, and that iron went into our furnace largely as Fe_2O_3.

We really knew—for we were electric-furnace people—very little about the condensation of zinc. As a matter of fact, my study shows that there is not very much known about large-scale condensation anyway, and so we followed the scheme that had been developed at Trollhättan over some 15 years, designing a condenser somewhat different from the one used there, making it safe from the operative view, which was of primary importance to us. We had seen their condensers blow out repeatedly on slight interruption of power supply. We are dealing here with condensers half the size of this room. We added an automatic safety device that flushed carbon dioxide into the condenser the instant there was the slightest change in pressure in the condenser. It worked very satisfactorily.

Before we were through with the two years campaign, however, we learned much about zinc condensers, and we made designs for liquid zinc recovery. Unfortunately they were not put into practice because of the closing down of the plant. We believe the new design will produce over half the metal in liquid form, and the rest in powder form.

A. J. Phillips.—I presume the charge was thoroughly dried?

---

[*] Works Manager, Irvington Smelting and Refining Works.

[†] Superintendent of Research, Central Research Laboratory, American Smelting and Refining Co.

W. S. Landis.—We used such drying facilities as were available and we tried hard to get it as dry as possible, but some moisture got into the furnace inadvertently. The plant was very much out of repair; the roof leaked, ores would get wet in transfer, and drying facilities were rather inadequate to cope with the tonnage this furnace smelted. We knew the very serious influence of moisture and just did the best we could with the facilities at hand. It was intended ultimately to dry thoroughly, just as we dry for all our electric-furnace operations in this country.

The condenser on the large furnace was in three compartments; that is, there were dividing walls between the compartments, forcing the gas to take a tortuous passage through them. In section 1 of the condenser we obtained 58 per cent of the total powder made. The zinc content of this powder was 81.4 total zinc, the metallic zinc 66.7 per cent. In section 2 we obtained 28 per cent of the total make of powder with the total zinc content of 85 per cent and a metallic zinc content of 72 per cent. In a furnace of such size, there is a tremendous amount of dust carried over, so these powders are contaminated by a very large amount of dust as well as with some oxidation of the powder during condensation.

Inasmuch as oxidized powder all went back to the smelting furnace automatically from the rotary, we did not at the start pay much attention to improving the quality of that powder. The extra kilowatt-hours did not mean so much in this preliminary work.

In section 3 we obtained only 13 per cent of the total make of powder, which carried 84.4 per cent of total zinc, 70 per cent in the metallic form. These figures differed somewhat with the variety of ore. We had practically equal quantities of powder in the three units, averaging a total zinc content of minimum 82, maximum 87; metallic, minimum 70, maximum 75.

A. Butts,* Bethlehem, Pa.—How was the reducing atmosphere maintained?

W. S. Landis.—No attempt whatever was made to control the atmosphere of the rotary furnace. The powder was charged as taken from the condenser. Because the powder is quite inflammable, it was caught in large, heavy, closed cans, taken over and dumped into a hopper above the rotary furnace and fed from the bottom by screw. It carried a considerable amount of entrapped air, but no attempt was made to go to the refinement of such things as producing a reducing atmosphere in the rotary, because we believed they were going to write the rotary out of the picture before we were through, in which event the powder would go directly to redistillation.

A. Butts.—Was there not considerable reoxidation?

W. S. Landis.—Yes, there was a considerable amount of reoxidization after the powder residue left the rotary furnace. It was a continuous operation, and practically all of the powder after leaving the rotary furnace burned to oxide before going back to the original smelting furnace. Very little zinc metal ever got back, even though there was metallic zinc in the unliquefied residue inside the rotary.

A. Butts.—The rotary was electrically heated also?

W. S. Landis.—Yes.

A. Butts.—And that did not redistill?

W. S. Landis.—No, it ran at a temperature just barely above the melting point of the zinc.

A. Butts.—How did you keep so low in arc heating?

---

* Assistant Professor of Metallurgy, Lehigh University.

W. S. Landis.—It was not an arc furnace. The smelting furnace was a three-phase arc furnace; the rotary was a resistance furnace in which 8-in. high-resistance carbons were set parallel with the axis about 8 or 10 in. away from the side walls, and they rotated with the furnace. A brush on a commutator structure took the power into the carbons. Those carbons lasted for a long time, but ultimately the abrasion of the metal would wear them through and they would break. It was a matter of a short time to slip out one and slip in another.

C. P. Linville,* Bound Brook, N. J.—What was the justification for the rotary furnace in the first place?

W. S. Landis.—That goes back of my history, and unfortunately I could find nobody that could tell me the early story. It seemed to be the keynote of this particular DeLaval process to condense the furnace product as powder and then liquefy that powder into metal in an additional step. Others have made other types of furnaces to perform the same liquefaction of the powder. In a DeLaval plant in Norway there was a tank on the bottom of the condenser with a curious wobbly motion that was supposed to reduce the powder and shake it into liquid metal.

The rotary was a fairly satisfactory unit, but it needed a great deal of mechanical improvement. Some means was required to take the discharged powder from the furnace back to the smelting furnace without letting metallic zinc again oxidize.

W. S. Landis (written discussion).—In a recent attempt to learn more of the early history of the DeLaval process, it appears that the inventor recognized the difficulty of producing and handling liquid zinc on a large scale from an electric smelting furnace. He apparently experienced this in his first experimental work and learned also of the same difficulty having prevented developments of the electrothermic process by others working in this field. Instead of being stopped by this very serious difficulty, he next attacked the problem of condensing all the zinc in the form of powder, believing that some contrivance could be developed to liquefy this powder. His answer was the rotary furnace as described.

A complete understanding of the principles of condensing zinc vapor in a smelting operation that slags the impurities and reduces all of the ordinary reducible oxides apparently was not a subject of comprehensive investigation, or at least has left no permanent records. It must be recognized that the process itself was designed originally to smelt ores that could not be treated in the ordinary retort. Such ores contain relatively large quantities of reducible oxides and at the temperatures of the electric furnace, which are probably of the order of 1500° C. or above, lime is reduced to carbide, silicon and iron to ferrosilicon, and in consequence the proportion of the oxides of carbon to zinc vapor are relatively much higher than when smelting a high-grade ore in the small retort. With our better knowledge of the effect of dilution on the condensation of metallic vapors and particularly of the adverse effect of water vapor and carbon dioxide, we must appreciate that DeLaval had a real argument for his principle of condensing as powder and then reworking the powder. It becomes an extremely difficult problem to handle on the scale in which even our small 5000-kva. furnace smelted, a mixture of powder and liquid zinc. Remember, this is a continuous operation and we cannot pull down our apparatus in the manner comparable to the operation of a small retort with its prolong. While we believe that the condenser design worked out on the basis of our experience will satisfactorily solve this problem, I cannot present operating data, for it was not installed before we were forced to abandon the work.

We did consider that we satisfactorily solved the problem of designing and operating the largest unit that has ever been projected for this industry and believe that it is quite feasible to build and operate a 10,000-kva. furnace. Also, that such furnace can be equipped with a condenser that will operate satisfactorily to produce all powder. We feel confident that by a change in the condenser arrangement a goodly part of the metal can be tapped out in liquid form and still permit handling the large quantities of powder that seem to be a necessary evil in electric-furnace smelting. We also believe that this quantity of powder can be continually reduced by better knowledge of the pretreatment of the ore, reducing the amount of the peroxides to the minimum, eliminating as far as possible the dragging in of entrained air, and certainly by more facilities for controlled roasting and for drying all elements that enter into the charge. We are not so optimistic, however, as to believe that we can completely eliminate the dusting of the charge into the vapor stream or reduce the oxygen problem to a point where we will make no powder. As a matter of fact, in units of this size it is very doubtful whether the cheapest and most convenient method will not be to take whatever a moderately complicated condensing system delivers and finish the operation in the redistillation furnace, since the operation of these large furnaces is not at all complicated. They require very little attention and service, because automatic control is so highly developed. While the power consumption is, as has been stated, approximately twice that of the electrolytic process, one must not lose sight of the fact that investment in electric furnaces is comparatively small as compared to the electrolytic process and the servicing much less burdensome. The question of power consumption in localities where such processes logically find their place is not at all the controlling factor.

---

* Metallurgist, The Calco Chemical Co.

St. Joseph Lead Company's Electrothermic Zinc-smelting Process

By George F. Weaton,* Member A.I.M.E.

Although an almost continuous campaign had been carried on by various experimenters since 1885 to find a commercial process of smelting zinc by electrothermic means, no commercial success was attained in the United States. The St. Joseph Lead Co., appreciating the theoretical possibilities of such a process, such as the ability to construct units of large capacity, quality control, and the possibility of treating complex and refractory ores, decided in 1926 that the process was worthy of further investigation, and in that year, at one of its southeast Missouri plants, began the development of the electrothermic zinc-smelting process according to the invention of the late Earl C. Gaskill.

Late in 1929 the process reached a stage of commercial significance, and in 1930 the erection of a modern electrothermic zinc smelter was begun, at Josephtown, Beaver County, Pa. The site is 3 miles from Monaca, which is on the main line of the Pittsburgh & Lake Erie Railroad, and a spur of the railroad has been constructed to the plant site. The site borders upon the Ohio River, which is navigable for 600 to 800-ton barges. This district was selected for the plant after an economic survey involving such questions as cost and availability of electric power, reduction fuel, transportation facilities, and the transportation charges on raw and finished materials, labor conditions, and taxes.

The initial unit of the plant was designed to treat daily 120 tons of 58 per cent zinc sulphide concentrates from the company's mines in St. Lawrence County, New York.

The plant equipment is housed in seven modern steel-frame buildings, and includes:

Roasting and Acid Plants

3000-ton concentrate storage.
Two Nichols-Herreshoff 21 ft. 6-in. diameter, 12-hearth roasters with usual cast-iron airshaft supporting chromium-alloy rabble arms and rabbles.
SO_2 gas purification system consisting of:
  One double-compartment hot-dust Cottrell precipitator.
  Cast-iron sinuous air-contact gas cooler.

Manuscript received at the office of the Institute July 30, 1936.

* Manager of Zinc Smelter, St. Joseph Lead Co., Josephtown, Pa.

Lead-water contact gas cooler, scrub tower.
Acid-mist Cottrell precipitator.
Large coke filter.
Two drying towers in series.

Clean SO_2 gas and acid system consists of:
Three Connersville gas blowers.
Two acid units (Fig. 1), each having: three heat exchangers; two vanadium pentoxide contact mass converters; one oleum absorber tower; one 98 per cent sulphuric acid absorbing tower; two 1000-ton acid-storage tanks.

Exit gases pass through one limestone neutralizer before final passage into atmosphere.

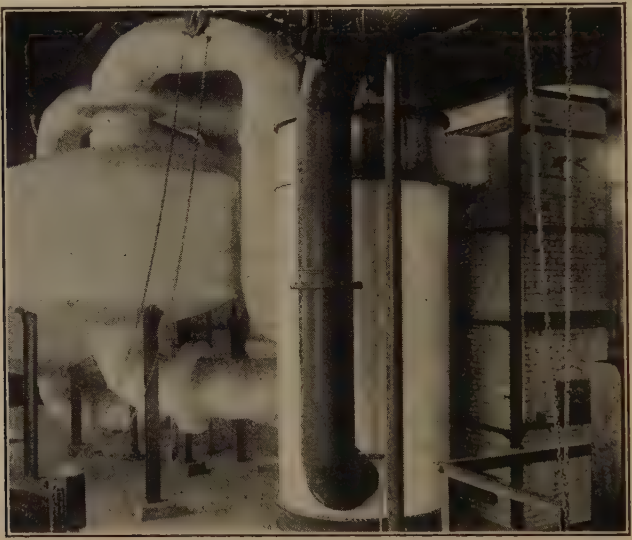


FIG. 1.—TWO ACID UNITS.

Roasted ore, or calcines, discharge to 16-in. water-cooled screw conveyor.
Elevator to storage bins.
Belt conveyor to sinter plant.

Sinter Plant

Storage bins for calcines, fuel, flux, reclaimed and waste zinciferous materials, etc.
Belt feeders under each bin, discharging to a common collect belt, which, in turn, discharges to a rotary drum mixer.
Mix elevator.
Tripper conveyors.
Three bins for sinter-machine charges.
Three rotary table feeders.
Three 42-in. by 44-ft. Dwight-Lloyd sintering machines.
Three gas-ignition muffles.
Three fans; 30,000 cu. ft. per min. at 14 in. water pressure.
Pan conveyors for handling hot sinter to two crushing rolls, one of which is in closed circuit with maximum and minimum trommel screens for sizing product.
Storage bin for product.

Coke-preparation and sizing plant.
Residue-treatment plant.
Belt conveyor for handling coke and sinter to furnace plant.

Furnace Plant

Eight storage bins for sized coke.
Eight storage bins for sized sinter.
Sixteen counterbalance constant-weight feeders.
Eight rotary preheating drums (Fig. 2), also showing furnace top.
Eight electric furnaces, 4 ft. 9-in. diameter by 36-ft. shaft (Figs. 3, 4 and 5).
Oxidation manifolds and oxide carrier ducts.
Electrical power needs are furnished by two 66,000-volt transmission lines, supplying current to two banks of transformers, each bank consisting of: three 1500-kva., 66,000/2300-volt, 60-cycle, single-phase units (Fig. 6).

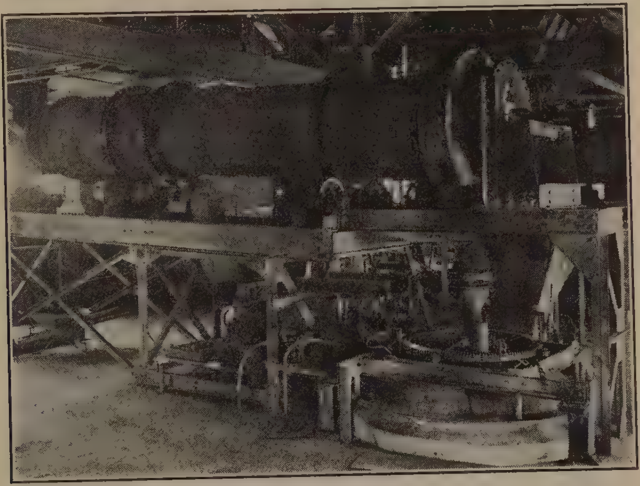


FIG. 2.—ROTARY PREHEATING DRUM.

Each furnace is served by three 2300/320/160-volt 1800-amp. single-phase transformers (Fig. 7). Minute regulation of furnace voltage is done by an induction voltage regulator in series with each transformer.
Each furnace's electrical system consists of three independent single-phase circuits. The electrodes of each circuit are 120° center to center and are spaced 24 ft. apart vertically. The electrodes serve only as charge contactors, the charge itself constituting a resistor of 57-in. normal diameter by 24 ft. long.

Oxide-collecting System

Each furnace is served by:
One fan of 30,000 cu. ft. per minute capacity when handling 250° F. gas at 8 in. water gauge and
One separator cyclone.
One hundred and fifty cotton filter bags (Fig. 8) are used, each 18-in. dia. by 45 ft. Each bag unit is shaken periodically by automatic shakers.
Oxide-collecting and transport equipment.

3

4

5

FIGS. 3–5.—ELECTRICAL RESISTANCE FURNACES.

Common to all units is the battery of fine-mesh shaking screens, packers, and so forth.

Ample storage facilities for finished materials.

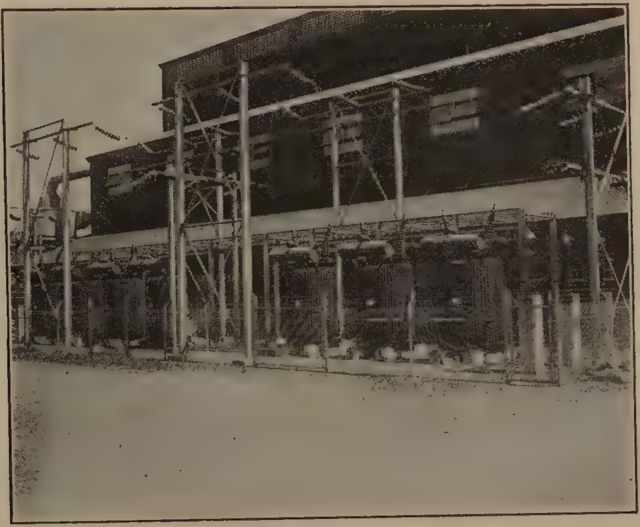


FIG. 6.—TRANSFORMER UNITS.

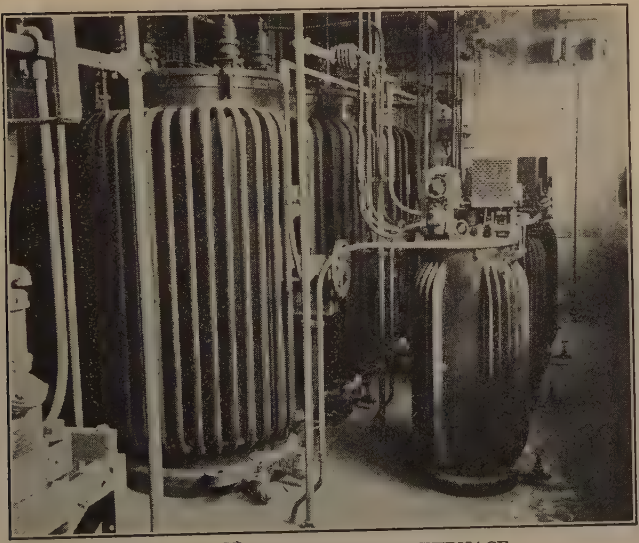


FIG. 7.—TRANSFORMERS AT FURNACE.

Maintenance and Research

In addition to the process equipment, the plant has a well equipped maintenance shop and a modern change house for the operators. In the mechanical department there is a well equipped machine shop, a tin shop, a carpenter's shop and a blacksmithing shop.

Laboratories and offices are housed in a three-story brick building, the top floor being occupied by the analytical laboratory, the product-control laboratory, the laboratory in which microscopic studies are made, and a general research laboratory and library.

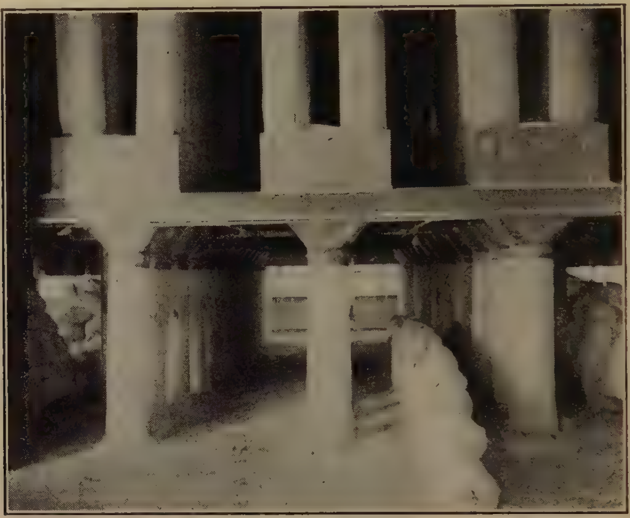


FIG. 8.—BAGHOUSE.

The second floor is occupied by the staff, accounting, purchasing, and engineering offices.

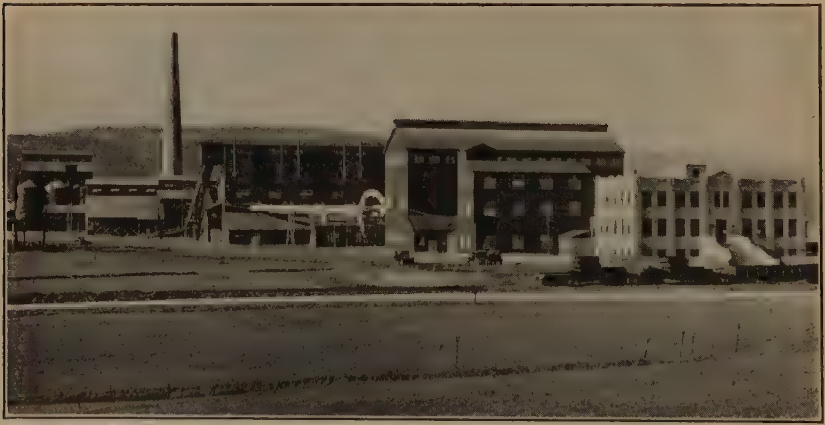


FIG. 9.—ST. JOSEPH LEAD COMPANY'S ELECTROTHERMIC ZINC-SMELTING PLANT.

The first floor contains the paint-research laboratory, the rubber-research laboratory and the constant-temperature, constant-humidity testing room.

The plant has its own pumping station, drawing water from shallow artesian wells near the Ohio River. A general view of the plant is given in Fig. 9.

THE PROCESS AND ITS OPERATION

Zinc concentrates, as received in boxcars from the company's mines in St. Lawrence County, New York, contain about 3 per cent moisture. The chemical analysis of the ore is: Zn, 57 per cent; Pb, 0.6; Fe, 6.6; Cd, 0.1; SiO_2, 1; CaO and MgO, 0.7. Cars are unloaded by a standard boxcar grain-drag scraper, which drops the concentrates into an elevator pit, from which they are elevated to the storage bins. The concentrates are drawn from the storage bins by apron feeders discharging upon a belt conveyor. Installed with the conveyor is a weightometer, which weighs all ore going to the treatment circuit via the Herreshoff roasters, which have chromium-alloy rabbles and rabble arms. Roaster temperatures are maintained up to 925° C. on some of the intermediate hearths. Sulphur is reduced from about 32 per cent in the original ore to about 1 per cent in the calcines, about 97 per cent of the sulphur being driven off in the roasters. Likewise, about 82 per cent of the lead and 50 per cent of the cadmium are driven off, being recovered by the Cottrell in the SO_2 circuit, and separately treated.

The SO_2 gases pass to the Cottrell at a temperature of approximately 550° C., some heat being recovered between the roasters and precipitators, by means of annular jackets through which passes the air required for the roasting process. The gases are further cooled by air-contact coolers and water-contact lead coolers, and enter the scrubbing tower at about 85° C. After passing through this tower the gases pass to the mist Cottrell, where sulphuric acid mists formed by conversion in the roasters, or from sulphates, are precipitated. The gases then pass through a large coke filter, which contains carefully sized coke, graded into filter beds. The lower layers consist of coke of considerable size, grading down to 20 mesh at the top layers. From the coke filters, the SO_2 gases pass into two 13-ft. drying towers in series, through which 63° Bé. sulphuric acid is circulated. The gases leaving the towers average 6 to 7 mg. moisture, and 0.03 mg. of H_2SO_4 mist per cubic foot. The gases then pass through the blowers, and the system changes from "suction" to "pressure" for passage through the heat exchangers and converters. The gases return to the heat exchangers, where the heat of reaction due to the oxidation of the SO_2 to SO_3 in the converters is utilized to heat the incoming SO_2 gases. The SO_3 gases then pass through the oleum towers, and on to the 98 per cent H_2SO_4 absorbers. A constant circulation of 98 per cent H_2SO_4 at a temperature of 80° C. over these units absorbs the SO_3 efficiently, the exit gases passing through the limestone neutralizer before making final exit into the atmosphere. Acid of 60° to 66° Bé., or oleum, may be shipped either by tank car or river barge. The acid in the absorber system is continuously titrated by means of a bridge-type titrimeter balanced to a standard strength of acid in a sealed cell. Titration is continuously recorded. Conversion averages about 96 per cent.

Returning now to the zinc circuit: The roasted concentrates, or calcines, fall from the twelfth, or bottom hearth of the roasters through a grizzly, pass a flap-gate air lock situated in an inclined chute, and fall into a 16-in. water-cooled screw conveyor operating at 5 r.p.m., which discharges into an elevator that discharges into a storage bin. This bin discharges the calcines upon an intermittently operated belt conveyor equipped with a weightometer for transfer to the storage bin at the sinter plant.

In the sintering process, inasmuch as an unusually hard sinter must be made, to stand sizing within definite limits for use in the furnaces, there is a considerable circulating load of so-called sinter fines, which are rejected from the minimum sizing screen. These, together with the calcine, coke fuel, reclaim and waste products, flux, etc., are thoroughly mixed and wetted to contain approximately 10 per cent moisture, then elevated to small storage bins from which the charge to each sintering machine is controlled by a rotating flat table under each bin. This table is driven by a variable-speed motor. Distribution on the sintering machine is done by the usual swinging spout. A bed thick enough to give a 10-in. thick finished sinter cake is carried on the sintering machine. The chemical analysis of the sinter is: Zn, 59.8 per cent; Pb, 0.06; insol., 8.18; SiO_2, 7.9; Fe, 8.8 and S, 0.1. The sintering machines discharge onto a heavy apron conveyor, which, in turn, discharges the sinter to a slugger roll, breaking the sinter cake to 4-in. size and smaller. Conveyors and elevators provide means for transporting the sinter to the maximum and minimum sizing screens, the oversize being crushed by a smooth roll in closed circuit with the maximum sizing screen.

Housed in the same building with the sintering apparatus is the coke-preparation equipment, which sizes the coke to practically the same size limits as the sinter, the process requiring that the entire furnace charge be sized within rather narrow limits.

The reduction fuel is a standard by-product-oven coke. The sized coke and the sized sinter are separately conveyed to the furnace plant, and stored in bins over the furnaces.

Also housed in the sintering plant is the residue-reclaiming apparatus where such values as can be reclaimed from the furnace-discharge residues are treated by screening and by magnetic separators, and returned to the sinter charge.

Perhaps the most interesting and unconventional part of the plant is the furnace plant, as this contains what are probably the largest electrical resistance furnaces in the world (Fig. 10). The furnaces have a bore of 57 in. and are 37 ft. over all in height. The charge for the furnaces is fed from the coke and sinter bins, by means of constant-weight feeders adjusted within a very few ounces per minute to a determinate feed and a definite ratio of coke and sinter. Before entering the furnace, the mixed charge is constantly fed into the preheating drum, where it is heated to a temperature of about 750° C. by means of natural gas. The preheated charge is fed into the furnace by means of a rotary distributor, which actually promotes a controlled segregation of the charge in the furnace. Leakage of the vapors and gases from the furnaces is kept very low by a small orifice through which the charge passes on its way from the preheater into the furnace. Each furnace contains upward of 25 tons of charge while in operation, and between the rotating discharge table and top electrodes the temperature is approximately 1200° C. About 18 hr. is required for

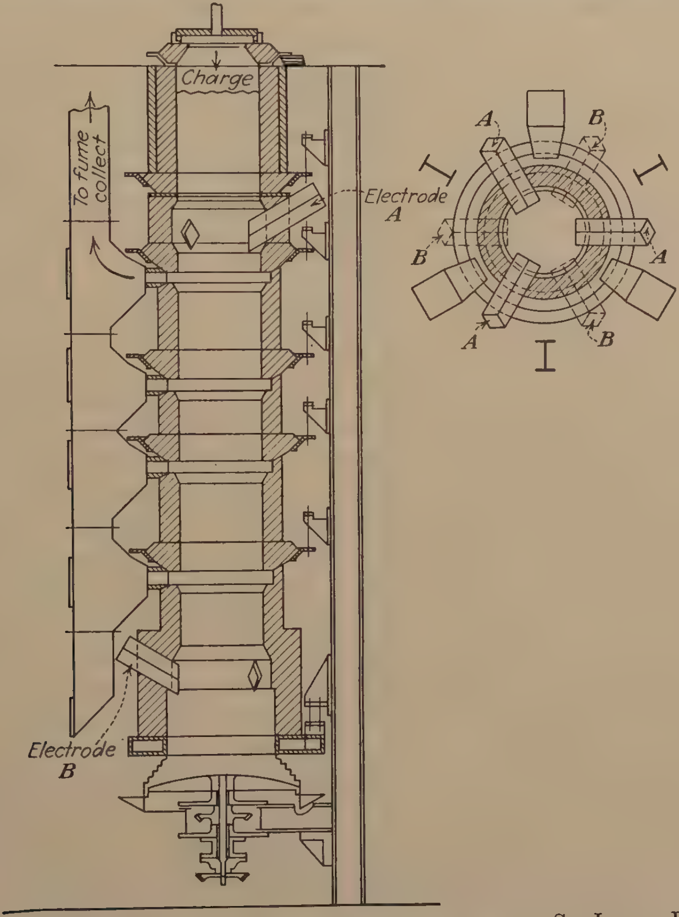


FIG. 10.—SECTION OF ELECTROTHERMIC SMELTING FURNACE, ST. JOSEPH LEAD CO.

the passage of the charge through the furnace, and each furnace requires about 29,000 kw-hr. daily. Voltage, which is subject to regulation according to the demands of the charge, averages about 265 volts.

The vapors and gas escape from the furnace through 12 openings, disposed three on each of four levels, within the electrode boundaries, which are 24 ft. apart vertically. Inasmuch as the smelting charge itself constitutes the resistor, it is necessary that the ratio of the zinciferous charge to the coke be maintained constant; that an excess of coke over that theoretically required for reduction be charged, the excess being reclaimed from the residues, and recharged; and that the sizing be fairly uniform in order that segregation in the furnace may be controlled and that second-class conductor characteristics within the charge may be prevented or modified. Assistance in the accomplishment of this is rendered by spacing several electrodes about the perimeter of the furnace, each of which is an independent single-phase electrical circuit between the top and bottom of the furnace. The furnace itself is of multiple-ring construction, each ring or section being not more than about 6 ft. high with a sealed expansion joint between adjacent sections. The bottom of the furnace is supported on a water-cooled ring, the worked-off charge being continuously taken from the furnace by a slowly moving rotary table discharging upon a pan conveyor. The gases and vapors from the furnace are oxidized immediately at the individual vapor outlets from the furnace, the rate of oxidation, which, in turn, controls the physical properties of the final product, being controlled by the amount of clean air permitted to contact the vapor stream at each outlet. The oxide is carried by the gas-air stream away from the furnaces, through the oxide fans, discharging into a large cyclone, where any carry-over of grit, such as minute pieces of coke, etc., is definitely separated out, the remainder passing to the baghouse. Approximately one square foot of bag area per cubic foot per minute of gases is provided. The bags are cotton, 18 in. in diameter and 45 ft. long. The zinc oxide clings to the interior of the bag, the gases filtering through. Bags are shaken by mechanical shakers every 30 min. The oxide drops into collect hoppers, from which it is collected and taken to fine-mesh (40 to 52-mesh) vibrating screens, after which the oxide is packed in 50-lb. paper bags, or barrels containing 250 to 300 lb. each. From the packers, the oxide is either placed in storage, for later shipment, or loaded directly into cars for immediate shipment.

The final product varies somewhat between different grades, depending upon the chemical constitution desired by the customer. However, a typical example might be taken as: ZnO, 99.4 per cent; PbO, 0.01 to 0.05; CdO, 0.002; Fe_2O_3, 0.002; total S as SO_3, 0.06 per cent.

Past methods used for the production of zinc metal from electric furnaces have not been very satisfactory from a commercial standpoint.

Present developments under way at the Josephtown plant are now showing great promise in this respect.

Plant Control

The control of the process described above depends largely upon laboratory results and is extensive, beginning with the analysis of the concentrates received from the mines, carried through every individual process in the plant, so that each part of the process obtains a known result for the government of later processing. Some results are reported to the plant every 2 hr. in order that the operations may be properly controlled. The analytical laboratory is well equipped to carry on any kind of analytical work that may be necessary in such a metallurgical plant, either for the control of the process or for materials that may be necessary to the process, constructional as well as those for processing. The process, under such control, produces high-purity products, and readily adapts itself to a wide variety of physical characteristics in the final pigment products.

The physical laboratory has a Zeiss microscope and photographic apparatus, projecting apparatus, colorimeters, suspension apparatus, mount-preparation system, development equipment, and so forth.

A well equipped rubber-testing and research laboratory is maintained for conducting tests to determine the physical or chemical properties of rubber compounds and the effect of pigments or other compounding ingredients on the properties of various compounds. All testing is done in a room with constant temperature and humidity.

A paint-research laboratory is maintained for the purpose of incorporating pigments into paints of various kinds and testing the properties of the pigments manufactured as well as the properties produced when these pigments are mixed with others generally used in the paint industry. Laboratory equipment includes the usual mixing and grinding equipment accelerated weathering-test machine, and a large outside 45° southern exposure test fence. Mobility, viscosity and other laboratory tests are made in the constant-temperature, constant-humidity room, the materials to be tested remaining in this room long enough to acquire a stable condition before testing.

Intermittent Zinc Distilling from Ore

By W. R. Ingalls,* Member A.I.M.E.

In choosing the unusual title given to this paper, in which the term "cyclic" might be substituted for "intermittent," my idea has been simply in respect of precision. We might say old method vs. new method, but that antithesis implies something of substitution that has not occurred and perhaps is not in sight. We may say horizontal retorts vs. vertical, but none of the older retorts are truly horizontal, and there are three different types of vertical retorts. Other complexities might be suggested. There is, however, a broad distinction between distilling that is accomplished in a periodic cycle, generally daily; and distilling that is accomplished continuously, irrespective of whether it be done in the vertical retorts of the New Jersey process or in the retorts of the Trollhättan process.

In offering a summary of the present state of the art with the intermittent process, I shall not have any idea of exemplifying it through descriptions of any single plants, but shall rather divide among the main steps of the process and outline what is best developed among them. In pursuing this thought, it will manifestly be impossible to make a composition that will exemplify the acme of good practice, for the latter will always be a function of the cost of labor, fuel, etc., which are widely variable. As of 1929, in respect of labor we might generalize the average plant wage in the Pittsburgh-Wheeling district of the United States at $5 per day; in Oklahoma at $3; in Great Britain at $3; in Germany at $1.75–$2; in Belgium and France at $1. With high labor costs the metallurgist will naturally use means of the nature of mechanization that with low labor would be uneconomical when capital charges are taken into account.

Nor may we from records of performance safely make positive deductions in respect of the efficiency of different types of furnaces unless they have been tested comparatively under identical conditions in the same works. We shall find gas-fired regenerative furnaces showing coal consumption from 1.2 tons down to 0.7 per ton of roasted ore, which may be ascribable to difference in the thermal value of the coal that is used or to differences in proportions of the parts of the furnace, which is something quite distinct from the principle of the furnace. Thus, we have

---

Manuscript received at the office of the Institute July 21, 1936.

* Consulting Engineer, New York, N. Y.

found that in increasing the charge of certain furnaces by substantial percentages we have not increased the requirement of gas from the producers, with consequently a reduction in the use of coal per ton of ore. Such experiences meant that we had started from a furnace of incorrect functional proportions and had brought them into better harmony.

Ore Storage

Zinc metallurgists who operate plants in close proximity to their ore supply, especially if the latter be a single mine, require less storage capacity than those situated remotely from ore supply, and especially those who receive ores from many sources. The arrangements for unloading ore, storing it, and perhaps making mixtures of it are not essentially different from those obtaining in the metallurgy of copper and lead. However, in zinc metallurgy I know of no present practice of mixing ores in beds, although I believe that has occasionally been done, and whenever the desirability of a mixture is indicated it is generally accomplished by drawing from separate bins. When ore is received in railway cars in winter it is often necessary to provide means for thawing.

Drying and Roasting

Flotation concentrates, arriving with about 10 per cent moisture, have to be dried and screened, and perhaps comminuted to break up lumps. In American practice revolving cylinders, internally heated, are used for drying. Also plate driers of the Lowden type. For screening the vibrating sieve is used. In some of our latest practice the preliminary drying is only partial, the process being completed on the top of the roasting furnace. From picking up the ore out of storage to delivery for distillation the passage of the ore is mechanical in the modernized American plants. In Europe there are also mechanized plants, e.g., Avonmouth and Rothem, but also there continues to be a good deal of shoveling and tramming, with good reason why there should be.

The latest American roasting practice is with furnaces of the McDougall type, from 8 to 16 hearths high. A 12-hearth furnace of this type with hearths 20 ft. in diameter inside may roast 50 tons of ore per 24 hr., burning down to 1 per cent sulphur. Survivals of the Hegeler furnace continue here and there. In Oklahoma, at plants that waste their sulphur gas, the Ropp furnace continues in use. All of the American furnaces are designed for large tonnage.

In Europe, at one of the plants of Giesche Spolka Akcyjna (in Poland) Wedge furnaces (McDougall type) are used. Examples of the Merton-Lurgi furnace are to be seen; for instance, at Duisburg. In general, European roasting is done in Spirlet (mechanical) and Delplace (hand-raked) furnaces, both of which are sometimes to be seen in the same plant. Their capacities are relatively small, say around 10 tons per day, but their efficiencies in respect of fuel consumption, degree of desulphurization and richness of sulphurous gas are high. With most of the good roasting furnaces at present coal consumption ranges from 20 to 10 per cent of the weight of the raw ore, varying according to type of furnace and the quality of the coal. The best practice is nearer the lower figure than the higher.

In such furnaces as those at Langeloth roasting may be done without the use of any carbonaceous fuel. It has been done at Donora by the introduction of brimstone into the lowest hearth, which, if not strictly autogenous roasting, is roasting accomplished without the use of carbonaceous fuel. Other departures from standard practice are the use of shower roasting (flash roasting) for Meadowbrook, W. Va., and at Deming, N. M., but this has not yet proved itself of common application.

At Avonmouth and Swansea, Great Britain, the desulphurization is accomplished by Dwight-Lloyd sintering machines of immense size, the ore being passed over them several times. At Swansea the charge per machine is about 70 tons of raw blende plus 350 tons of return sinter, the proportion of the mixture being therefore about 1:5. In the final product the sulphur is reduced to 0.25 per cent. About 95 per cent of the total sulphur is concentrated in the roast gas, averaging 5.2 per cent.

Ordinary roasting practice is furthermore now to be distinguished between preroasting and dead roasting, the former being stopped at about 8 to 10 per cent sulphur remaining, and the latter being continued down to 1 to 2 per cent, according to whether the further processing is to be by the Rigg method or by the Baelen method. If sintering is not to be done as preparation for subsequent distilling the desulphurization is performed as perfectly as is economically possible. As preliminary to electrolytic extraction, the metallurgist preserves some sulphur as sulphate in the ore to make good the loss of sulphuric acid in subsequent treatment and preserve the acid balance of the plant.

SINTERING

A few zinc distillers continue to charge loose calcines, but in the majority of plants treating sulphide concentrates, both in Europe and America, the ore is sintered preliminary to distilling. This is done for the sake of better desulphurization, which may be carried as low as 0.25 per cent sulphur, and for the sake of improved results in distilling, which follow principally from: (1) the better desulphurization, and (2) betterment of reduction, etc. This improvement may have been of the order of 4 per cent; i.e., recovery of zinc may be raised from 86 to 90 per cent with reference to the same ore and same practice. However, this is not to be interpreted as a broad generalization, for a plant that was already enjoying good roasting would naturally experience less improvement by virtue of sulphur elimination than a plant wherein the roasting was not so good.

In general, we had confirmation of the classic theory that one unit of sulphur holds back two units of zinc.

On the other hand, the introduction of sintering carried with it some penalties. It introduced another process, involving the use of heavy machinery requiring attention, power for driving and upkeep. It introduced also a new outlet through which zinc might escape, and in a way not easy for recapture, the volume of gas being so large. In American experience the loss of zinc by reduction and volatilization is negligible, even when the Baelen process is being used, and the major loss is by dusting, which can easily be mastered by suitable mechanical means. I am acquainted with a European practice, performed on American lines, in which the total loss of zinc in roasting plus sintering has been reduced to as low as 0.5 per cent. I do not think that we get as low as that anywhere in America, but during the last 10 years the loss of zinc under this head has been very much reduced.

In sintering there are two major practices of general use; and two more that are of special use; that is, employed in single plants or by single operators. The major processes are the original Rigg method, in which the ore is preroasted down to about 9 to 10 per cent sulphur and is then sintered. In the United States this is used only at Bartlesville. The other process is the Baelen method, in which the ore is dead roasted, or nearly so, and then is sintered with admixture of 4 to 6 per cent carbon.

In both of these processes the gas that is drawn off from the wind boxes was originally so low in sulphur dioxide as to be useless for manufacture of sulphuric acid and with the Rigg method there was consequently a considerable loss of sulphur. At Avonmouth, however, by the use of a special seal (1928) covering the joint between the pallets and the wind boxes, dilution was reduced and gas of sufficiently good strength for sulphuric acid manufacture was obtained. This was improved (first at Uethemannhuette in Upper Silesia, and later at Avonmouth) by making the pallets slide on a well greased track, mechanically oiled. The annular form of Dwight-Lloyd, used in Germany, permits a good seal to be made.

The two special processes are those that are used at Avonmouth and at Overpelt. At Avonmouth raw ore is desulphurized and sintered by repeated passes, to which reference has been made hereinbefore under the head of roasting. This process was previously tried at Herculaneum, Mo., but there it was not found to offer any advantage. At Avonmouth it has been thoroughly successful. This simply illustrates that the same process may be good in one place and not good in another, the determinative factor being economic conditions and manner of application.

In the Overpelt process the ore is preroasted down to 5 to 7 per cent sulphur and is then moistened with water to which a small proportion of ferrous sulphate is added. The mixture is kneaded and extruded as threads about 4 mm. in diameter and 20 mm. long. After drying, these threads are delivered to the sintering machine, which is able to take a bed about 20 in. deep—manifestly much more than can be charged with fine ore. The purpose of the Overpelt process is obviously to increase the porosity of the bed. The sintering is so expedited that the production of 213 lb. of sinter per square foot of useful grate area per hour is realized. Desulphurization is carried to less than 1 per cent total sulphur, and a gas containing 5 to 5.5 per cent sulphur dioxide is obtained and used for making acid.

In the United States the only sintering apparatus used is the Dwight-Lloyd, straight-line machine, which functions like an endless belt, the pallets dumping at one end. In Europe the Dwight-Lloyd straight-line machine is used extensively, but there is also a considerable use of the Schlippenbach, an annular machine, in which the pallets move in a horizontal plane above a ring of wind boxes and trip for their discharge in a blank segment.

There are some differences in control of the operation. Some metallurgists prefer to produce a hard, porous sinter, while others prefer a soft, friable sinter. This means that in one instance the ore is more extensively fritted than in the other and of course the nature of the gangue of the ore has a good deal to do with this. One of my friends in Europe thought that he had better reduction from Rigg sinter than from Baelen, made from the same ore. There are also differences in practice in respect of the degree of crushing the sintered cakes, the carefulness of sizing, the return of fines, etc. The metallurgical changes that may occur in sintering have not perhaps been carefully studied. There may be some beneficial prereduction of iron oxides. Reduction of cadmium, volatilization and loss of it obviously occur. By the addition of salt to the charge lead may be chloridized and volatilized, the ore being thus purified. Such modifications have been the subjects of patents and of limited application.

Dust Collecting

In roasting with multiple-hearth furnaces of the McDougall type the escape of dust attains large proportions, and with flotation concentrates it may rise to 8 to 10 per cent of the weight of the raw ore charged. The dusty gas escaping from the furnace is commonly led through a brick chamber in which a good deal of the dust, perhaps 50 per cent, settles by gravity, and thence through a Cottrell precipitator designed for hot gas, for of course the clarified gas must reach the Glover tower at a temperature high enough for it to function properly.

In a few plants dust collection is effected by means of improved Siroccos, which are highly efficient as dust collectors from cool gas but in the course of time operate with impaired efficiency on hot gas containing lead fume. Nevertheless, chamber acid has been made at Langeloth for the last seven or eight years with no other means of dust removal.

In roasting a blende containing cadmium and lead a large part of the former and a considerable part of the latter are volatilized and recaptured in dust and fume. In roasting an ore containing 0.25 per cent cadmium, the cadmium may commonly be recaptured in the flue dust up to a tenor of 4 per cent, all of it as water-soluble sulphate. Lead is precipitated in the Cottrell fume as sulphate. These products may become sources of cadmium and lead, respectively, as by-products.

Conveying, Cooling and Mixing

The calcines discharged from the roasters are conveyed away mechanically by closed conveyors, good forms of which are the Jacoby, the well-known endless screw, and the push-plate. The calcines may be discharged into a cooler, a long cylinder revolving in a tank of water, in which their temperature may be so reduced that they may be safely dumped into the bins or tanks from which the sintering plant is fed. Up to, and through, the sintering plant all operations are performed in enclosures within which dust is confined or from which escaping dust may be recaptured. By such means the loss of zinc has been reduced to a mere fraction of what it used to be, and over-all recovery is consequently improved.

The calcined or sintered ore, crushed and screened, is mixed with the desired proportion of reducing carbon and perhaps the addition of about 1 per cent of sodium chloride. The function of the latter and the practice in respect of it will be discussed hereinafter. For reducing coal a good many materials are employed, largely according to availability and cost; e.g., anthracite fines or duff, coke breeze, a mixture of coke breeze and slack coal. Major considerations are not to have too much volatile matter, the minimum of ash and the minimum of sulphur. There is no sense in taking pains thoroughly to desulphurize the blende and then to put sulphur back through the reducing coal. As a reducing agent there is some difference in the activity of certain carbons. Charcoal would theoretically be beneficial.

Reducing coal performs the double function of reducing zinc oxide and also acting as a sponge to hold up molten slags and so protect the retorts. For the latter purpose a large excess over the theoretical requirement is commonly employed, but in the practice of the last 10 to 12 years this has been immensely cut down, especially in American practice. In most of our works the amount of reducing coal used is now 30 per cent or less. In some European practice the proportion is still as high as 45 per cent. In speaking of these percentages we always mean the wet weight of the material rather than the dry weight of its carbon.

The mixing is now done mechanically, in substantially the same way as the mixing of concrete. The same type of machine is employed for both. In American practice the mixture is deposited in cars that are trammed to the furnaces, from which it is shoveled directly into the retorts. In some European practice the charge is deposited on the floor immediately in front of the furnace, and if blue powder and other between products are going to be mixed with it that is about the only way to proceed. With mechanical mixing the responsibility of the mix-room foreman is large, for thorough mixing is important. Even after that has been accomplished there is the possibility of resegregation in subsequent handling, considering that the mixture is composed of materials of quite different specific gravity.

Distilling

In general practice all over the world distilling is performed in a cycle of 24 hr., of which the maneuver (the operations of drawing spent residue, the scraping of condensers, recharging, replacing condensers, replacing broken retorts, etc.) occupies from 5 to 2 hr., the latter being exceptionally low and 4 hr. being about the lowest of good practice in general. After gas has been turned on, about 2 hr. is required for the performance of preliminary reactions following which the condenser flames become purple and then begin to show tinges of green from burning zinc. The time of active distillation is therefore about 18 hr., whereof the first quarter is a waxing period and the last quarter is a waning period. Manifestly, the greater the celerity of performing the maneuver, the longer is the period of active distilling, but of course the temperature gradient is very much of a correlative factor in all of this. The cycle might be prolonged, from 24 hr. to 30, 32 or 36, and improved recovery with less breakage of retorts be obtained; and, indeed, in America in the recent years of depression, some of metallurgists have done just that, and with the benefits indicated by theory. This has been economically indicated only by the possession of a surplus of furnaces. It would be clearly uneconomical to provide a surplus of furnaces at original cost for such an objective.

Furnaces

With but few exceptions the zinc-distilling furnaces of the world are now gas-fired and heat-recuperative in one way or another[1]. Gas is derived from *gazogenes*, which are installed in batteries near the furnaces, or perhaps in a central plant from which it is piped to all furnaces. The *gazogenes*, or producers, themselves are of standard types and as they are employed in great variety they need not be described here, nor even mentioned. The Muensterbusch plant at Stolberg has a central gas production. So does Rose Lake, at East St. Louis. There may be others that I do not recall. Palmerton to a considerable extent employs gas from its spiegeleisen blast furnaces, and Rosita uses coke-oven gas, both of which come to the same thing at a central plant. In the American Southwest natural gas is employed. Distilling furnaces have been fired with petroleum and with coal dust, but those have not been common practices and are of interest only as precedents.

---

[1] The term "recuperative" is here used in its broad sense. In technical vernacular, however, we commonly use this term as descriptive of furnaces effecting heat exchange between currents moving in constant directions and describe as regenerative furnaces those in which the direction of currents is reversed at intervals.

Except for our American natural-gas-fired furnaces, almost all distilling furnaces are heat-recuperative, indirectly if not directly. The Hegeler furnaces of the United States deliver their products of combustion through waste-heat boilers for generating the steam required in the plant, and the credit for that reduces the furnace quotient to a reasonable figure, perhaps as low as one ton of coal per ton of ore. The steam generation is usually short of the plant requirement for power and may have to be boosted by accessory coal-dust firing. The waste gases from the Hauzeur furnaces, at Auby, also pass through steam boilers. So also have I seen steam boilers following regenerative furnaces, but that is unusual and ought not to be necessary if the checkerworks are of adequate capacity, which is not always true.

Of the truly recuperative furnaces the continuous, countercurrent system has surrendered to the alternating, reversing, or Siemens system. The experience at Palmerton, where the two types were operated side by side, and where the change was definitely made about 1924, may be regarded as having settled this question that for a long time was debatable. As compared with the Siemens furnaces that were substituted for them, they used about 30 per cent more coal and let their gases waste to chimney at 560° to 600° C. vs. 360° C. At about the same time Siemens furnaces were substituted at Muensterbusch for the recuperatives that had long been used there.

Of the reversing regenerative furnaces there are several major types, but their number is not large in respect of differences of principle. In one major type there are four checkerworks, two for air and two for gas. In another major type there are only two checkerworks, which are only for preheating air, and the gas producers are then preferentially put close to the furnace so as to deliver the gas with as much as possible of its initial heat. On the basis of these fundamental differences furnaces will be distinguished according to the movement of the gas currents within their combustion chambers.

The original Siemens furnace (spoken of before as the Auby furnace) has four checkerworks, and the gas and air issuing from their ports rise and descend alternately over a middle wall. Furnaces of this type are used at Rose Lake, Peru and Palmerton in the United States; at Stolberg (Birkengang works), Hamburg, and elsewhere in Europe; indeed, quite generally in Germany. The Welzer furnace has four checkerworks, from which the gas and air reverse in alternate directions. This furnace is used at Overpelt and Lommel, in Belgium, at Uethemannhuette in Upper

Silesia, and elsewhere. The Tanier furnace that was developed at Sclaigneaux is a modification of the Welzer and is used extensively at other plants in Belgium and the north of France. The Van Gulck furnace has checkerworks for preheating air only. The gas and air reverse over a middle wall, as in the Auby furnace. The Van Gulck furnace is used at Avonmouth, at Swansea and at Montagne.

The Dor-Delattre furnace, which was developed at Budel, also has checkerworks only for preheating air. It is distinguished from all other distilling furnaces in that instead of having the checkerworks in the inferior structure the Dor-Delattre has them at the end of the superior structure and conveys the gas and air through longitudinal canals above the combustion chamber instead of beneath it. In the Berzelius works at Duisburg the furnaces are of similar design. Asturienne has one of the Dor-Delattre furnaces at Auby and four at Aviles (Spain), and it is noteworthy that when Vieille Montagne rebuilt Flône and Valentin Cocq a few years ago it adopted this form of furnace. The Dor-Delattre design permits the checkerworks to be built of adequate capacity, only at the expense of floor space, whereas when they are built in the lower part of the furnace they are subject to certain limitations and frequently are not made large enough. The Dor-Delattre system may have some other distinct advantages.

Except the Dor-Delattre furnace, all of the regenerative distilling furnaces have their checkerworks in their substructure. As to their superstructure it is now difficult to classify sharply between the Belgian and the Rhenish type, for whereas some furnaces exist in their purity there are many that share the characteristics of both types. The Rhenish furnaces of Europe have commonly from 216 to 288 retorts of 2 to 3 cu. ft. internal volume, arranged in three rows, the two fronts being divided into closets, or windows, each containing the condensers of two retorts. The Belgian furnace has retorts of smaller volume, say 1.5 to 2 cu. ft., and more of them; the Dor-Delattre has 432, arranged in six rows, but five-row furnaces are more common. In the United States our Hegeler furnaces have commonly 608 retorts in four rows. The Neureuther-Siemens furnaces have commonly 800 retorts in five rows. In general the tendency in the United States has been to reduce the number of rows to four, especially in the Hegeler and natural-gas-fired furnaces. American metallurgists generally stick to the cylindrical retort, but some have adopted retorts of elliptical cross section, and in certain instances their axes are as large as those of the Rhenish retort. In all American furnaces the inner ends of the retorts rest on ledges projecting from the middle wall. Such construction also obtains extensively in Europe, but with the pure Rhenish furnaces there is no middle wall, the arch springing from face to face, and the inner ends of the retorts rest on the ledges of a perforated wall or banquette, and with retorts of great length, up to 72 in., and even

78 in., an intermediate support of the same nature is provided. In American practice retorts longer than 54 in. are seldom to be observed, although we do go up to 60 inches.

Even with the purely Belgian furnaces the *devanture* (the front structure) is deeper in Belgum than in America; i.e., the condensers do not stick out so far beyond the plane of the face of the furnace. The Dor-Delattre furnace has a shield that can be pulled up or down, more or less like a Venetian blind, protecting the front of the furnace against drafts of air. The same thing was in the mind of E. C. Hegeler when he surrounded his entire furnace with a curtain of sheet iron, which also is to be seen at Danville. The Rhenish furnaces usually have hoods extending along each front of the furnace, connecting with a main, through which noxious gas and fume are drawn off. Escaping zinc oxide, chloride, etc., may be recovered from this system, but trials in the way of doing so have demonstrated that it is not worth while. The prolongs themselves are effective collectors, and from a European zinc distillery there does not hang the great cloud of white smoke that hovers over many American plants.

The essential requirements of a distilling furnace are economy of fuel, uniformity of temperature, and such arrangement of inlets and outlets for gas, air and combustion of products that they do not become clogged with dripping slag, dust, etc. Economy of fuel results from the proper proportion of retort space to combustion chamber, and of checkerworks, together with avoidance of excess of secondary air. Uniformity of temperature is accomplished by the proper distribution of combustion and restriction of the alternating travel of the burning gas. In any reversing, regenerative furnace, whether the currents be up and down, down and up, or end to end, there will be a neutral zone midway, where the furnace temperature will be slightly inferior. In the old Siemens furnace this zone will be above the middle wall, where there may be a fall of 50° C. in the furnace temperature. The metallurgist aims to achieve an even glow of white heat throughout the combustion chamber. In furnaces of the Welzer type (end to end reversal) I suppose that the neutral zone is reduced to the minimum, for the gas and air enter alternately through ports almost up to the median transverse line.

Plant Layout

Modern zinc-distilling furnaces are built entirely aboveground, except for their foundations, and are attended from an upper floor. The residues drop into side pockets, from which they slide into cars to be trammed away. Sometimes a mechanical conveyor is provided for that purpose. American furnaces of the Hegeler type and those in the natural-gas fields still have ash tunnels under them through which residues are removed.

In the European plants the furnaces are commonly lined up end to end with the retort tempering ovens between them, several furnaces being grouped in a hall. Such a layout exists at Palmerton, but elsewhere in the United States the furnaces are laid out in parallel, each in its own house, except in the natural-gas fields, where there are two per house. In the vernacular of those districts, the separate furnaces are called "stoves," a pair of them still being regarded as a "block."

Most zinc-smelting plants having been evolutionary, there are to be observed in them unbalances among functional departments and irregularities in equipment, such as furnaces of different types, different sizes of the same type, and different forms and sizes of retorts in the same furnace. Sometimes metallurgists consider that they have good reasons for variations; i.e., elliptical retorts in the lower three rows and cylindrical in the upper two may be held advantageous for certain furnaces and certain ores. The ideal plant, in my opinion, has all functions in balance in multiples of two and all parts alike in each department. Thus, there may be four roasters, four acid systems, two sinterers and eight distillers, with no bottlenecks between the several departments.

Retorts and Condensers

The essential features of the process of distilling in the intermittent way are the retorts and condensers, which are made in a separate factory of the plant that in the American vernacular is called the "pottery." From this the retorts, after seasoning (drying), are delivered to the distilling furnaces day by day as required, and, after tempering in a near-by kiln, wherein they are brought slowly up to bright red heat, or as nearly to furnace temperature as possible, they are drawn out for making replacements in the furnace.

The batch for making retorts is a mixture of burnt clay (chamotte, grog) coarsely crushed and of raw, fat clay, in proportions of 50:50 to 60:40. The chamotte forms the skeleton of the concrete, so to speak, and the plastic, raw clay is the binder. The more chamotte, the stronger is the retort; the more fine clay, the less porous is it. A physical balance has to be struck. There are also chemical considerations in so far as the character and composition of the clays, together with other materials, may be adjusted to character of the gangue of the ore, from which slags will result. If the gangue be siliceous the retort should also be strongly siliceous; if the gangue be basic, either from iron or lime or both, the retort should be aluminous or inert.

In accomplishing such purposes, substitutions for parts of the chamotte and clay are made. A common substitution almost everywhere in Europe is the introduction of coke dust, which should be as fine as possible, to the extent of 10 or 15 per cent, but in America this is scarcely ever used. The coke dust tends to give the retort somewhat of the qualities of a graphite crucible. Another substitution is the introduction of some granular quartz, for the purpose of making the retort more siliceous. However, inasmuch as quartz has a higher coefficient of expansion than clay, the grains of it tend to have a rupturing effect when the retort is heated. This is counteracted by adding the silica in the form of flour, which during the last 10 years has been widely adopted in American practice. A mixture might be, for example, 25 per cent chamotte, 25 per cent silica flour and 50 per cent clay. Such retorts have done very well with our siliceous Joplin ore. Another innovation has been the use of carborundum retorts; e.g., 65 per cent carborundum and 35 per cent clay, which has occurred both in Europe and America and has offered the theoretical advantages of better heat conductivity and long life. With the retort of unchanged diameter, other conditions remaining the same, the better conductivity may increase zinc recovery by 2 per cent; or the diameter of the retort may be increased (as at Amarillo and Rosita) and heavier charging may be accomplished with undiminished zinc recovery. The life of the retorts may be tripled. With ferruginous ores and furnaces fired with producer gas, however, adventures with carborundum retorts in some instances have been quite disastrous, the retorts suffering corrosion from the outside as well as from the inside. Naturally, the carborundum retorts are much more costly than the clay retorts. The carborundum retort is therefore a utensil of occasional use rather than general use.

With all types of retorts, it is obvious that the thinner the wall the better the conductivity. Practice has everywhere for a long time settled upon a wall thickness of about 1 in. and a butt thickness of about 2 in. As among the ordinary clay retorts, the graphitized retort and the silica-flour retort, I have been unable to discern any material difference in conductivity by pyrometric observations or in the way of zinc recovery apart from the matter of breakage.

In cross section and dimensions the retorts that are used at present are of wide variety. The commonest form of the Belgian retort is circular, from 7½ to 8 in. in diameter. Extensively used also are retorts of elliptical cross section. While we so describe them, they are really two half circles joined by a rectangle, which gives them straight sides. Dimensions may range from 6½ to 7½ in. for the short axis (width) and 9 to 12 in. for the long axis (height). As a general principle, reduction in width improves penetration of heat, reduces retention of zinc in the residue and improves recovery. Height is not a factor in this. Reducing the width of a retort from 8½ to 8 in. brings about a striking improvement, from 8 to 7½ further improvement, but not so strong, from 7½ to 7 and from 7 to 6½ still further improvement, but at diminishing rates. In going below 7 in., there is increased difficulty in charging.

Besides the circular and elliptical cross section there are also the muffle-shaped (not much in use now) and the oblong (with rounded edges), the latter to be much commended. Different forms and dimensions may be produced by simply changing the die of the press.

In length, inside dimensions, retorts run generally from 48 to 72 in. In European practice they are longer than in American, for we seldom go beyond 54 in. The ability to charge well and mechanical strength are of course governing factors. We may consider the retort as a hollow beam, supported at each end and carrying a uniformly distributed load of perhaps 250 lb. at temperature of perhaps 1500° C., constructed of fragile material.

The cross section of the retort and its length compound into cubic measure, or internal volume or capacity. In use in the United States are retorts ranging from 1.5 cu. ft. (old) to 1.75 cu. ft. (common) to 2.2 cu. ft. (unusual). In Europe retorts of 2 cu. ft. are now common and in some Rhenish furnaces they are of 3 cu. ft. In Belgium there has been in recent years a tendency to increase capacity for the sake of increased charging. During 1933, in one plant, dimensions of 1500 × 190 × 220 mm. were increased to 1700 × 195 × 270. At another plant a length of 1.8 m. was adopted, its retorts then having an internal volume of 2.6 cu. ft. Retorts of length of 1.9 m., or 76 in., are of record.

In all modern plants the retorts are molded under a pressure of about 150 atmospheres by means of the Mehler or Dor-Delattre hydraulic presses, which are improvements of the original Dor press. The molded retorts are transferred to the drying rooms, wherein they season by gradual loss of their water. As freshly molded, they contain from 12 to 15 per cent water and are introduced into the drying rooms at a temperature of 60° to 70° F. With a gradual rise in temperature after the first 15 days their water content will have been reduced to about 2.5 per cent at the end of 30 days; to about 1 per cent at the end of 60 days; and to about 0.3 per cent at the end of 90 days, the temperature being gradually elevated to something like 130° F.

Practice varies in respect of the speed and duration of drying. Some metallurgists use their retorts after a month of drying, while others insist upon three months, or four months, with a slow increase of temperature. We have records of substantial increases in retort life as a consequence of care and patience in this particular. At the best, a retort of clay or other refractory material is an imperfect vessel, being subject to porosity, to microscopic cracks and to differences in strength when regarded as a beam. Retorts may be tested by closing them with an airtight cover, pumping air into them under pressure, as into an automobile tube, and painting the exterior with a solution of soap. Loss of pressure, which is always rapid, correlates with development of soap bubbles on the exterior, which are uniform if the retort be homogeneous, but irregular if there be microscopic rents, which let the air out very quickly. In order to counteract porosity, the retorts in European practice are commonly dressed inside and out with a slurry of powdered glass and soda, or similar composition which upon burning glazes the retort. Such glazing is seldom done in American practice.

Condensers are made from mixtures of clay as for retorts, but inferior grades are used, and old retorts, cleaned of slag and crushed, often take the place of chamotte. In the United States, most condensers are of the simple conical form and made by a machine that forces a conical mandril into a conical mold containing the requisite quantity of clay. A belly may be produced in the tube by cutting out a gore from the larger end and drawing the two sides together; which, of course, is handwork. Condensers have been made by machine-molding, with a diameter at the large end greater than that of the interior diameter of the retort to which it is to fit, and reduced to fit by inverting the molded condenser into a conical ring, which is called "crimping." This produces a bottle-shaped condenser and may increase the interior area from 300 sq. in. to about 360. Many different shapes of condensers have been, and are now, used. The more complicated they become, the more handwork is required. The old Rhenish condenser was a substantially rectangular tube, rounded at the top. The Dagner condenser, used in Upper Silesia, is a composition of rectangular tubes.

In length the Belgian condensers vary from 18 to 24 in., while the Rhenish and Silesian condensers were about 36 in. long. Recently, some of the Belgian metallurgists have increased the length of their condensers, even to as much as 35 in. This subject is complicated and will best be discussed further on when we consider furnace operation.

Condensers are sometimes burned prior to use and sometimes are used unburned. Either way the breakage of them is large and, as we shall see subsequently, this is a very important matter. The breakage is partly mechanical, from careless handling, and partly chemical. The latter is evinced by splits occurring while the condenser is in place and not being handled, such as a longitudinal rent or a ring-rent that may let the nose fall off. Specks of iron oxides in the clay and the action of hot carbon monoxide may have something to do with this.

Coal Consumption

The records are generally not comparable, for they fail to take into account the value of the coal, the grade of the ore and other variables, among which are both the type of furnace and the proportions of the furnace. The thermal efficiency of the best furnace is so low that large changes in the charging may be made without affecting the quantity of coal burned in the producers, but greatly altering the quotient of pounds of coal per ton of ore. We have found that out from experience. Not even is the temperature of the products of combustion escaping from a regenerative furnace to the chimney a true gauge, for though we might think that a temperature of 300° C. looks good the volume of the wasting gases may be too high, which always it will be if the excess of a secondary air be too great.

Our practical deductions therefore are quite empirical. A Hegeler furnace distilling ore of 70 per cent grade with gas produced from coal of 13,000 B.t.u. may give a figure of 1½ ton per ton of ore, which with a steam credit of one-third may be reduced to 1 ton net. On the same grade of ore a regenerative furnace with coal of 12,000 B.t.u. may give a quotient of 1.1 ton, which perhaps might be reduced by heavier charging. With the best regenerative furnaces and the best practice coal quotients of 0.9 and 0.8 are rather common. I know of one furnace that with coal of 13,000 B.t.u. used only 0.72 over a month. These figures are very different from those of the old direct-fired furnaces that used to consume 3 or 4 tons of coal per ton of ore. However, when we look at the New Jersey continuous furnace and see quotients like 0.5, we are conscious that we still have some distance to go. We should not overlook that in intermittent distilling there is a period of 6 hr. or so, including the time of the maneuver, when the furnace has to be kept hot without doing any directly useful work, wherefore 0.8 ton in one case and 0.5 in the other are not perhaps very much out of harmony[2]. We may also be cognizant that the intermittent furnace, having to rework a large proportion of intermediate products, is required to do the same work twice over.

Reduction and Condensation

The zinc oxide of some ores reduces more easily than that of other ores. One of the advantages of sintering has been improvement in that respect. The activity of the carbon employed as reducing agent also plays a role. Apart from such differences, the controlling factors in reduction are temperature and time, which are correlative. Time may be increased by shortening the maneuver or extending the cycle to something more than 24 hr. Temperature is limited by the durability of the retorts and the stability of the furnace. In European practice there are maximum temperatures of 1400° to 1500° C.; in American practice, 1300° to 1400°, but rarely as high as the latter. These are temperatures in the combustion chamber; inside of a clay retort with 1-in. wall the temperature will be 100° to 200° lower. The front ends of the retorts, resting on shelves, will not be so hot as further in, consequently there will be poorly reduced ore in that place. Carborundum retorts, because of their superior conductivity, run hotter toward the front than do clay retorts.

When the reduction of zinc begins and the vapor starts to come over, the preliminary reactions have not been fully completed and the gas is high in carbon dioxide, which as the temperature falls in the condenser acts oxidizingly on the droplets of zinc and produces blue powder, from which we are never entirely immune although in the course of time the gas discharges with only about 1 per cent carbon dioxide. The blue powder, which to the naked eye is merely an impalpable dust, really is composed of microscopic globules, which show frostings and sproutings of zinc oxide that prevent the globules from coalescing. Amelioration of this is the rationale of the addition of about 1 per cent of sodium chloride to the ore. Volatilizing it is intended to dissolve the zinc oxide as chloride or oxychloride and so clean the pellicles of zinc and allow them to melt down. Probably that occurs. Anyway we find zinc chloride in the prolong dust. This spells a loss of zinc, though perhaps no more than will be suffered in redistilling a larger quantity of dust. At all events, the addition of sodium chloride to the ore is not essential. Meadowbrook, before it went over to continuous distilling, regularly ran without it. Of course the furnacemen have to get used to a different condenser flame, one that is deprived of the sodium coloration.

---

[2] In using this illustrative quotient for the continuous furnace, I am having in mind data prior to utilization of the gas escaping from the condenser.

The observation may be made that in American practice it is common to "stuff" the condensers; i.e., partly to close their outlet, allowing the gas to escape through a small hole, which is kept open by constant "spiessing." This gives a certain internal pressure in the retort and condenser, and if this becomes too much, through inattention, the gas and vapor may break out through the luting around the joint between condenser and retort. When prolongs are used on the condensers they are open. If the prolong is on tightly the gas escapes through only the small hole near its end. In some European works there is an excellent practice of putting a small sheet-iron cuff around the nose of the condenser, protecting it from breakage.

The subject of zinc condensation is not very well rationalized from the practical point of view. The Dagner condenser of the Silesian furnace is soundly conceived, being a long pipe folded in zigzag and enclosed in a closet whose temperature can be controlled, but it is not easily applicable to a furnace of more than one row of retorts or to a practice of daily taking down and putting up. The Belgian and Rhenish furnaces with condensers registering with the retorts are restricted in length by thermal conditions—which is not, perhaps, of great importance inasmuch as lengthening of nose does not add much to superficial area; and restricted as to girth by lack of room and difficulty in getting at the joint for luting, etc. However, there is a certain latitude whereof advantage is taken. Swansea uses a condenser of 415 sq. in. internal surface attached to a 2.2-cu. ft. retort.

Nevertheless we see a good deal of practice wherein the density of charging is increased and the grade of the ore is increased and the volume of the retorts is increased while the condensers remain unchanged, although they are required to condense more zinc. In respect of this, it is not so much a matter of the total pounds to be delivered in the 18 hr. of the period as it is the maximum pounds per hour.

The Europeans take care of these conditions by their use of prolongs, which are efficient condensers of zinc as dust. Owing to their higher temperatures of driving, a good deal of vapor is put into them and collections are made from them of the order of 3 to 5 per cent of the zinc in the ore charged (occasionally as high as 15 per cent). Europeans are averse also to having ore of too high a tenor in zinc, and experimentally did not take kindly in Belgium and France to Joplin ore of 60 per cent grade (raw). However, Giesche, in Poland, has lately been distilling Silesian blende of that grade and Waelz fume of 70 per cent grade.

In American practice, even with such high-grade ore, we do not with our milder driving put much zinc into the prolongs, which have been used only exceptionally, and only up to the first draw of spelter.

Charging

With the Silesian furnaces after the discarding of the knee-form condenser, and with the Rhenish furnaces always, the condensers were fixed in place, the opening into the retort under them being closed by a plate, which was taken down for raking out the residue. The new charge was introduced through the condenser. With the Belgian furnaces the condenser registered exactly with the retort, and for raking out residue and recharging of course it had to be daily taken down and put up again. In charging the Belgian furnaces, the ore mixed with coal was thrown in by means of a scoop shovel. In charging the Silesian and Rhenish furnaces, the ore mixed with coal was introduced through the condenser by means of a long-handled, long, narrow spoon, which was inverted when it had been pushed far enough into the retort.

There was something to be said in favor of the apparently clumsy method of charging through the condenser. Because of the depth of the closets, a throw would be long. The idea prevailed among many furnacemen that they could charge the retort more fully by this method than by throwing. The condensers did not have to be taken down and put up again until they were ready to be discarded, which saved some labor in the maneuver. On the other hand, charging through the condenser was slower than by throwing. With a three-row Rhenish furnace in a Silesian works the filling of a single retort required 3½ min., but for throwing in the charge the time was only one-half as long. Of course, either of these times look slow in comparison with what chargers do in American works.

The practice of keeping up the condensers and charging through them by spoon prevailed extensively until recently but during the last 10 years most works have gone over to the Belgian practice of making a condenser that fits the retort, taking it down and putting it up every day, and filling the retort by throwing in the charge.

The charger has one of the very responsible positions. His work is arduous. The idea of substituting mechanical charging for hand-charging has consequently been engaging. Numerous mechanical chargers have been designed and applied on a regular working scale. These may be generalized as slingers and shooters, the former being designed to throw in the charge and the latter to shoot it in. In American practice such chargers have been used at Palmerton and at Rose Lake. In Europe there have been many applications, the most noteworthy of which is at Rothem, in Belgium.

In general, the conclusion has been, I think I am safe in saying, that there was no material gain either in labor saving or in efficiency of performance, and that when first cost, upkeep, etc., are considered, they are not worth while. At Rothem, however, the Dor-Delattre charger, which shoots in the charge, has continued in regular use for a good many years. It puts 13,000 lb. of ore into 210 retorts in 20 min., and reduces the total time of the maneuver to 2 hr., leaving 22 hr. for distilling.

Density of Charging

During the last 15 years in American practice, and more recently in European practice, much attention has been given to increasing the density of the charge, which means increasing the number of pounds of ore introduced per cubic foot of retort volume. Accomplishment of improvement in this direction depends on several factors, among which are: (1) specific gravity of the ore; (2) proportion of reduction material mixed with the ore, for obviously the less reduction material the more room there will be for the ore; (3) the care with which the charge is thrown in, avoiding cavities; and (4) the force with which the charge is thrown in. An expert charger can throw a shovelful of charge into the retort with such force as to break its butt. A mechanical charger can put a quantity of ore into a given retort that in comparison with the best hand-charging is almost unbelievable, and can do it so densely that a strong man is unable to drive in the spiess rod. Such excessive density of charging may introduce more zinc into the retort than, after reduction and vaporizing, the condensers are able to handle; therefore recovery of zinc may be impaired rather than improved. Up to this critical point, however, increase in density of charging is beneficial from the standpoint of metallurgical reactions in the same way that a briquetted charge may be beneficial. A full discussion of this subject would unduly extend this chapter. My thought is simply that increase of density up to any known limit is advantagous, but all of the elements must be coordinated in order to get the full benefit of it.

In American practice, charging sintered ore weighing about 105 lb. per cu. ft., mixed with 30 per cent of reduction coal, wet weight, we charge about 55 lb. of ore per cu. ft., or 110 lb. in a retort of 2 cu. ft. capacity, and here and there that figure is exceeded.

Furnace Charging

Although density of charging per retort has a good deal to do with the charging of the furnace as a whole, the subjects are two different things, although this is commonly overlooked, and the two expressions are commonly confused. The zinc that is reduced and vaporized is not wholly condensed directly as spelter. We may get 65 to 70 per cent of it as direct spelter; the remainder as zinc dust, blue powder, which must be redistilled. Besides the blue powder that is skimmed from the ladles and recovered from the prolongs, there are other between-products that must be redistilled, including the imperfectly distilled ore remaining in the front end, perhaps 10 per cent, of the retort, which in American vernacular is called the "sample" (for no good reason) and in the Belgian vernacular is called the "gueules" or "throats"; the cleanings from the condensers; the cleanings from the pans on the floor along the front of the furnace, etc. In good practice these collections may aggregate 20 per cent of the weight of the original charge; in careless practice they may run to 30 per cent.

In American practice this entire collection is described as blue powder. With the Hegeler furnaces it is recharged into the sections of retorts at the chimney end of the furnace. With the Siemens furnace it is charged into the uppermost row of the roasters. In Europe it is more generally mixed with the ore. I am acquainted with occasional practice where it is reserved and redistilled in a separate furnace. Whatever be the method, it occupies furnace room, increases the fuel and labor quotients per ton of ore and subjects a certain portion of the zinc to a renewed opportunity for loss.

Translated into terms of furnace charging, if a furnace of 600 retorts, or 1200 cu. ft., should be charged fully at the rate of 55 lb. per cu. ft. it would receive 72,000 lb., but if only 480 retorts can be charged with ore the total is 52,800, and if only 420 can be charged with ore the total is 46,200, and all the quotients are altered accordingly. The furnace charging is therefore a composite of the density of charging and the proportion of between-products.

These illustrative computations are exclusive of old condensers, which may be crushed and added to the charge or may be crushed and jigged and the concentrate added to the charge; or the concentrate may be accumulated and be distilled separately. All of these practices are to be observed.

Loss in Distilling

In Great Britain ore from Broken Hill assaying 50 per cent zinc (raw) with an irony gangue is distilled with a recovery of 90 to 92 per cent of its zinc. In Upper Silesia ore assaying 60 per cent zinc (raw) with a limey gangue, mixed with Waelz oxide assaying 70 per cent zinc is distilled with a recovery of 90 per cent. In Belgium, where miscellaneous, custom ores are treated, the average recovery is probably around 90 per cent. In all of these instances the ores are sintered. In the treatment of similar ores in the United States, I doubt whether 86 per cent is anywhere bettered. From Joplin ore, 58 to 60 per cent zinc (raw), we can and do recover 90 per cent. In these citations I am having annual averages in mind, and so naturally include recovery from old condensers. Such figures were being attained eight years ago. It does not seem to be easy to raise them materially. However, 92 per cent has been attained over a period of months and may possibly be maintained over twelve. These percentages are better than those obtained by electrolytic extraction save with ores of exceptionally high zinc solubility, excluding what may subsequently be salvaged from the slag following residue smelting. Of course retort residues may also be beneficiated in a similar way.

TABLE 1.—*Recovery and Loss of Zinc in Distilling Roasted Joplin Ore*

Recovery and Loss	Percentages		
Direct spelter	66.0		66
Zinc in ladle skimmings	16.0	Aggregating 22.5 between-products redistilled, yielding	
Zinc in condenser cleanings	2.5		
Zinc in pan cleanings	1.5		
Zinc in sample	2.5		20
Total spelter			86
Total initial recovery	88.5		
Zinc in ore residue	6.0		
Zinc escaping from condensers	2.0		
Zinc retained by condensers	1.65		
Zinc absorbed in retorts	0.35		
Zinc escaping through chimney	1.5		
Total primary loss			11.5
Total secondary loss			2.5
Total accounting	100.00		100.0

It is important to examine the ways in which loss of zinc occurs in distilling. Most important is its retention in the residue. Apart from that the losses are scattered. Absorption by retorts. Retention by condensers. Escape from condensers (if prolongs be not used). Filtration through retorts and leakage by retorts breaking, contributing to loss up the chimney (which is a loss very difficult to measure). There is some recovery of zinc from dust and fume depositing in checkerworks and settling on furnace tops, but both are troublesome.

An illustrative analysis of the recovery and loss of zinc in distilling roasted Joplin ore of about 70 per cent grade (after roasting) appears in Table 1.

The residue amounted to 30 per cent of the ore charged and assayed 14 per cent zinc. Nearly half of its zinc content was in oxidized form capable of being reduced. Daily loss of condensers was 15 per cent. Each discarded condenser contained about 7 lb. of zinc. By crushing and jigging, about two-thirds of its zinc could be recovered in a concentrate assaying about 70 per cent zinc, of course at a certain cost. This salvage is not included in the analysis of recovery and loss. The absorption of zinc in retorts is computed on basis of daily loss of 3.33 per cent (correlating with 30-day life). Each discarded retort carried away about 6 lb. of zinc. The loss of zinc escaping through the chimney is computable only by difference. It is more or less proportionate to the percentage of breaking retorts.

In Table 2 is a similar analysis of the same ore distilled: (1) as ordinary calcine and (2) as sintered calcine.

Table 2.—*Analysis of Joplin Ore*

Recovery and Loss	Distilled as	
	Ordinary Charge, Per Cent	Sintered Charge, Per Cent
Direct spelter	66.0	69.8
Blue-powder spelter	20.0	20.0
Total spelter	86.0	89.8
Zinc in ore residue	6.0 } 7.2	3.8 } 5.0
Zinc in blue-powder residue	1.2 }	1.2 }
Zinc retained by condensers	2.3	2.3
Zinc absorbed in retorts	0.5	0.5
Zinc escaping from condensers	2.1	0.5
Zinc escaping through chimney	1.9	1.9
Total accounting	100.0	100.0

The sintered ore experienced less loss of zinc by failure to reduce and by better condensation. The rate of condensation between the first and second draws was about 5 lb. per condenser per hour, the condensers having about 300 sq. in. of internal area.

I think that many zinc-distilling balance sheets will be more or less in harmony with this. With the use of prolongs the loss of zinc by escape from the condensers is practically excised. The loss of zinc by absorption in the retort is negligible. Old condensers generally assay about 30 per cent zinc, and the more the rate by breakage, the more do they carry away. Although the larger part of such zinc may be regained there is additional cost, both for milling and distilling.

With regenerative furnaces there is some recovery of zinc from the checkerworks when they are cleaned. In one plant this averaged 25 per cent zinc by assay and figured to 0.3 per cent of the zinc in the ore charged. Cleaning of the tops of the furnaces also gives a product assaying about 25 per cent zinc and accounting for 0.2 per cent. This dust is used in the mixtures for stuffing and luting condensers, and so finds its way back into the blue powder.

Metal Drawing

Spelter was drawn from the Silesian and the original Rhenish condensers only once during 24 hr. With the smaller Belgian condensers more draws were necessary, and even more as grade of the ore increased. In American practice, four draws are the common daily routine.

In quantity the draws vary according to the period, correlating with the activity of the distilling. Table 3 is more or less typical.

TABLE 3.—*Typical American Draws*

Draw	From Calcines, Per Cent	From Sinter, Per Cent	Time
First	23	22.2	2.30 p.m.
Second	29	29.4	7.00 p.m.
Third	29.6	29.0	12.30 a.m.
Fourth	18.4	19.4	6.30 a.m.
	100.0	100.0	

This introduces the subject of the temperature gradient, or what may be plotted as the furnace thermograph. This is more or less variable according to the operating conditions. Beginning at 1000° to 1050° C. with "gas on" and immediately after completion of the maneuver, it may rise in a straight line, or in a slightly arched line, with different speeds. With a rapid rise the maximum, 1330° C., may be attained at 11.30 p.m. With a slow rise it may not be attained until 2.30 a.m. The rate of reduction naturally correlates with the thermograph. After the maximum has been attained it is held level for several hours, or until the distilling of zinc is distinctly on the wane, nearing its end, when the temperature is allowed to fall to save retorts from being "butchered" when there is no longer an endothermic reaction occurring within them.

The temperatures that I am suggesting herein are as registered by Seger cones inside of an open retort. It is common practice to record furnace temperatures in that way. Also temperatures in the combustion chamber by means of recording pyrometers. Even when the latter are used, however, the Seger cones afford a valuable check.

In European practice the spelter is commonly drawn into small ladles by hand. With some furnaces the lowest row of retorts is so near the floor that nothing else could be used. In American practice a large kettle carried on a car on the rails in front of the furnace is universally employed. The spelter is drawn directly into this. When the kettle is full the metal is skimmed and then is poured into a row of molds. There is no question as to the superiority of this method.

Retort Residue

After distilling has been completed, the spent residues must be withdrawn, usually by hand, but machines have been found useful in some plants, without becoming of general application. In some American practice a water pipe is introduced into the retort, letting out a little water, which immediately becomes converted to steam and blows out most of the residues. With the fluffy residues from Joplin ore that does very well, but with a slaggy or "gummy" residue it simply has to be hoed out.

Some lead from a leady ore goes over into the spelter. A considerable proportion of it may be recovered by gravity refining, but that which is retained by the spelter adds to the weight of the latter and realizes the spelter price for good ordinary brands. Most of the lead and all of the gold, silver and copper remain in the residue. If the silver content be high, which has occurred with some ores, e.g., Butte & Superior, the entire residue is passed on to the lead smelter. In general, however, the residue is jigged for separation of its lead, together with the silver carried by it, and the concentrate is passed on to the lead smelter. A large part of the lead production of Belgium originates in this way.

The recovery of silver, lead, etc. from the residue from distilling may therefore be as high as from the lixiviation residue from electrolytic extraction. In general, however, the recovery is less, for economic reasons. The question of costs is determining. Of course the higher deleading of ores in the original concentrate plays an important part in this. The zinc smelter does not get ore as high in lead as formerly.

In American practice there is relatively little recovery of lead from retort residues, but they are sometimes jigged and washed for recovery of undistilled zinc, unburned coal, etc. The Waelz furnace is also occasionally employed as a scavenger. In general, however, it is too big for the quantity of residue produced even in a big distillery. The Dorschel furnace, recently introduced in Germany, may be better fitted for such work.

Labor

In the management of the zinc-distilling furnace there are two systems, one commonly practiced in America, wherein the furnace crew of 30 or so is divided into groups of specialists, each group performing a single operation; the other, which is in general practice in Europe, wherein the furnace crew, which is always relatively small, is divided into squads, each of which takes charge of the operation of a part of a furnace, a half or a quarter, collectively performing all the operations of the maneuver. After the maneuver has been finished the furnace passes into the charge of the fireman and the metal drawers, who work in the same way by either system.

I hesitate to make economic comparisons, for the reason that so many modifying conditions enter into the problem and shall confine myself to a few suggestions. In 1928 an American furnace charged with 24 short tons of ore was attended by a crew of 30 men, inclusive of gas producers but exclusive of those who removed residues from the ash pockets. This figured to 1.25 man-day per ton of ore. Contemporaneously one of the most modern of the gas-fired furnaces in Belgium received a charge of 11 short tons of ore and had a crew of 20 men, which figured to 1.8 man-days per ton. The American furnace had 608 retorts; the Belgian had 320; the volume per retort being about the same in each instance. The Belgian furnace had prolongs; the American did not. The extraction of zinc was higher with the Belgian furnace than with the American. I am merely beginning to suggest some of the factors that qualify comparisons.

Furnace Campaigns

In modern practice distilling furnaces are frequently under continuous fire for five years. Shutting down to reline is costly and the longer the campaign, the less the cost of upkeep per ton of ore. The failure in the end is generally of the middle wall. The arch also may suffer. A furnace is of record as having been under fire at Cherryvale for 10 years[3]. A Dor-Delattre furnace has been in use at Auby for 15 years with only one relining (1936).

Refining

Cadmium and lead both go over with zinc. Cadmium concentrates in the first draw of spelter. Lead is higher in the later draws. Some grading is accomplished by keeping them separate. Drawing into the large kettles in American use, there is some equalization of the molten metal, but even so there may be wide variations in the draws from different parts of the furnace, especially from our Hegeler furnaces that have so pronounced a drop in temperature. I have seen comparative analyses of spelter, section by section, that were astounding.

By remelting the spelter it can be equalized and excess of lead settles out. This is the simple process of gravity refining. Refining may also be done by redistilling, but that does not get rid of cadmium. The New Jersey process of reflux refining enables ordinary spelter to be raised to four-nine grade and in this respect puts the old process of intermittent distilling on equal terms with electrolytic refining.

---

[3] This furnace finished a 10-year campaign in 1917, having produced 29,136 tons of spelter out of approximately 60,000 tons (raw) of Joplin ore.

SUMMARY

In this presentation of the present state of the art of intermittent, or cyclic, distilling, I have confined myself to the practical physics and have abstained from going into the economics, beyond here and there a few intimations. Consequently I have avoided comparisons among the several methods of zinc production that are now in use; viz., intermittent distilling, continuous distilling with external heating, continuous electrothermic distilling and electrolytic extraction. Any comparison among them would introduce a consideration of many conditions that are widely variable, and would extend a study to the proportions of a treatise. The operation of Giesche Spolka Akcyjna in Poland is the only one with which I am acquainted where the same ore, or substantially the same, is beneficiated by intermittent distilling and by electrolysis under substantially identical conditions. In this the consumption of firing coal per ton of ore is less in the furnaces than in the steam boilers that make power for the tankroom, etc. On the other hand, the quantity of labor (man-days) in the leaching, plating and melting departments is substantially less than it is on the distilling furnaces. This is a broad generalization that I think will be found true everywhere.

Recently built steam stations operate at about 11,500 B.t.u. per net kilowatt-hour of output, with a total investment cost to get power on outgoing lines of about $100 per kilowatt. With the use of 2000 kw-hr. per ton of ore (which naturally varies according to the tenor of zinc in the ore) an electrolytic plant might require 2000 lb. of coal of 11,500 B.t.u. grade. A distilling furnace may be operated with 2200 lb. of coal of the same grade (including reduction coal). For the production of steam, however, we must add the manufacturing cost, including capital charges, and might experience a cost of 0.5¢ per kilowatt-hour under the most favorable conditions.

So far as my acquaintance extends, the requirement of power in electrothermic distilling is rather more than in electrolytic extraction.

In our old process of intermittent distilling we have had during the last eight years a remarkable improvement in execution, not so much through invention as through improved understanding of physical principles, which has occurred both in Europe and in America. As I look over individual plant records of both continents during the last 10 years, the improvement is no less than amazing. The strain of severe economic conditions has been contributory to this.

In the last annual report of the Overpelt-Lommel company it was stated that although economic conditions were at their worst in 1934 the company achieved an operating profit by virtue of plant improvement. The Overpelt and Lommel works, which formerly had an average monthly capacity for the production of 2900 tons of zinc in June, 1934, actually produced 4000 tons, although no additional furnaces had been erected. I have no information as to how this was accomplished, but increase in density of charging, trimming of reducing coal, reduction of percentage of between-products, and increase of volume of retorts might bring about such a result if those factors were not up to top notch to begin with.

Reduction of Zinc Ores by Natural Gas

By H. A. Doerner,* Member A.I.M.E.

The process for smelting zinc developed several centuries ago is still in use. Through the experience accumulated over this long period of time, details of the process have been perfected until there is little opportunity to make any further improvement except by a radical change in method. Such a change was accomplished by the process recently developed by the New Jersey Zinc Co. The process to be herein discussed is a still more radical departure, which has been developed to large-scale laboratory operation by the Metallurgical Division of the U. S. Bureau of Mines[1].†

The reduction of zinc oxide by carbon is a highly endothermic reaction, which requires temperatures in the range 1200° to 1400° C. for even a slow reaction rate. The transfer of the heat of reaction through thick fire-clay walls, the high radiation loss in the type of furnace used, and the practical impossibility of recovering or using the combustible products of the reduction (CO) cause a deplorable waste of fuel. With the one exception mentioned, all zinc smelting is done in small retorts manually charged and discharged. Attempts to mechanize these operations have been only partly successful, and there seems to be no way to avoid or improve the uncomfortable conditions in which the work is done.

The reduction of zinc oxide by methane has a relatively high reaction rate at 1000° C. At this temperature most ore residues do not sinter, and it is possible to use metal retorts. These factors make gaseous reduction especially adapted to a continuous operation and compared to reduction by carbon make possible: (1) higher rate of reaction at lower temperature, (2) more nearly complete extraction of the zinc, and (3) much better utilization of fuel and reagent.

Although the reaction between methane and zinc oxide requires 105,900 calories per mole, compared to 86,860 cal. in the carbon reduction, it is obvious that much less fuel will be required to supply 105,900 cal. through $\frac{1}{8}$ in. of metal at 1000° C. than to transfer 86,860 cal. through 1 in. of fire clay at 1300° C. Moreover, the gaseous products of gaseous reduction (CO and H_2) can supply 183,430 cal. by complete combustion.

Manuscript received at the office of the Institute June, 1936. Published by permission of the Director, U. S. Bureau of Mines.

* Metallurgical Division, U. S. Bureau of Mines, Pullman, Wash.

† References are at the end of the paper.

In a thermodynamic study of the chemistry of zinc smelting, Maier[2] made a preliminary study of the chemistry of reduction of zinc oxide by methane, pointing out that the following reactions, the limits of which could be theoretically predicted, were important:

$$ZnO + CH_4 = Zn(gas) + CO + 2H_2 \qquad [1]$$
$$CH_4 = C + 2H_2 \qquad [2]$$
$$ZnO + CO = Zn(gas) + CO_2 \qquad [3]$$
$$ZnO + H_2 = Zn(gas) + H_2O \qquad [4]$$

It was further predicted that reactions 2, 3 and 4 might be troublesome, and, in fact, were sure to be so at higher temperatures, but that thermodynamically reaction No. 1 should proceed nearly to completion not far from 925° C. Thermodynamic considerations were shown to be powerless to predict the rate at which such reaction would occur, and the desirability of experiments to determine this point was emphasized.

PRELIMINARY LABORATORY TESTS

Acting upon this recommendation, laboratory tests were made[3] to determine whether or not the rates involved are such that reaction 1 will predominate and take place with sufficient speed to make commercial application feasible.

The apparatus consisted essentially of a vertical retort and condenser, constructed of silica glass, with electrothermic heating and the usual equipment for regulating and measuring temperatures, flow of gas, etc. (Fig. 1, *R.I.* 3091). The results only of these tests are of interest here, and may be summarized as follows:

1. The rate at which reaction 1 takes place is appreciable at 900°C., and it increases rapidly with increasing temperature. In the temperature range 975° to 1000° C. the rate at which zinc distills from an ore calcine (with substantially complete utilization of the gas) is considerably higher than is obtained from retorts by standard practice (comparing zinc distilled per unit of retort volume). The thermodynamic predictions as to the limits of the reaction were thus fully confirmed.

2. Thermal decomposition of methane by reaction 2 takes place to some extent where the gas enters the reaction zone. Most of the decomposition occurs before the gas has reached a high enough temperature to react with zinc oxide. Above the reaction temperature (900° C.) no carbon is formed, unless there is a local deficiency of zinc oxide. The amount of thermal decomposition can be calculated from the ratio of hydrogen to the oxides of carbon in the gaseous products of the reactions. Reaction 1 gives a ratio of 2.0; in laboratory tests the ratio averaged 2.05, indicating that thermal decomposition under normal conditions is not a major difficulty.

With natural gas containing about 15 per cent of the higher homologues of methane, the minimum ratio is about 1.85. The homologues are less stable than methane, more thermal decomposition takes place and the ratio of hydrogen to oxide of carbon in the gaseous products is about the same as when pure methane is used. Therefore methane reduces zinc with a high factor of utilization, and California natural gas has an equivalent effective reducing power.

3. The side reactions 3 and 4 were not studied in detail, but the amounts of CO_2 and H_2O in the gaseous products is a measure of the net effect of these reactions. The CO_2 content of the gaseous products varied between 0.4 per cent (at 925° C., low gas velocity) and 1.3 per cent (1000° C., high gas velocity). No water vapor could be detected under any conditions.

4. Reoxidation of zinc, due to the reversibility of equations 3 and 4, is important. Since the equilibrium concentrations of CO_2 and H_2O increase with increasing temperature, the reverse of these reactions takes place when the gases are cooled to condense the zinc. The higher the temperature of reduction, the larger the proportion of the zinc reoxidized. In the usual retort practice reoxidation customarily produces "blue powder." In the laboratory tests, the product of reoxidation was a yellow, crystalline zinc oxide, which deposited on the retort wall at a zone having a temperature of about 850° C.

5. The reduction process was tested with pure zinc oxide and methane, also with natural gas and a calcined zinc concentrate. The latter required a pretreatment at 800° C. with a reducing gas (H_2 or H_2 and CO) to eliminate sulphates; otherwise the condenser became fouled with sulphides. Rate of reaction and utilization of the gas were about the same with either pure or commercial reagents.

6. The zinc metal condensed readily in a clean, coherent, and relatively pure spelter.

From these results it was apparent that reduction of zinc ores by natural gas had the following advantages over ordinary smelting methods:

Cost of a Reagent.—On the basis of its reducing power (as given by equation 1), 12,000 cu. ft. of methane will reduce one ton of metallic zinc. In present practice about one ton of coal is required for the same purpose. Methane, if completely utilized as a reagent, at 10¢ per 1000 cu. ft. is thus equivalent to coal at $1.20 per ton.

Thermal Economies.—The most economical retort furnaces require about one ton of coal as fuel for each ton of zinc produced. In such a furnace, the endothermic heat of reduction is equal to about 11 per cent of the heat supplied[4], and it is not feasible to use the gaseous products of reduction for fuel.

The combustion of the H_2 and CO resulting from reaction 1 will produce more heat than the endothermic requirements of that reaction, and in the type of apparatus suitable for methane reduction these gases can easily be utilized to heat the retorts. The following factors, peculiar to methane reduction, may make a high efficiency possible:

a. Low operating temperature. The heat required to maintain a temperature of 900° to 1000° C. is very much less than that necessary for the present retorts at 1200° to 1400° C.

b. Thermal conductivity of retorts. The thick clay retorts are poor conductors of heat. At temperatures below 1000° C. metal retorts are a possibility.

c. Thermal conductivity of the gases. The gaseous products of methane reduction contain 50 per cent H_2, and equal parts of CO and zinc vapor. Hydrogen is an excellent conductor of heat.

d. Continuous countercurrent operation. Batch methods are thermally inefficient. Continuous countercurrent operation is not only feasible but practically essential when methane is used for reduction.

e. Radiation losses. The thin front walls of present furnaces radiate large quantities of heat. Retorts using gas for reduction can be enclosed in furnaces having well insulated walls on all sides.

Maintenance.—The replacement of retorts and furnace linings is a big item in the cost of operation. At temperatures below 1000° C. the life of refractories is much greater, the ore will not fuse, stick to, and damage the retorts.

Labor.—With continuous, automatic feed and discharge of ore, and the use of gaseous fuel, labor is a small item and working conditions are very much better.

Recovery.—Low temperature, which eliminates fusion of the ore residues; continuous, countercurrent operation; low concentration of CO_2 in the gaseous products; all these favor high recovery. With the use of carbon for reduction, the zinc vapor is expelled from the retort by the pressure of the gases evolved, which decreases as the reduction proceeds, so that the last portions of zinc cannot be profitably extracted. Using gas for reduction, the spent ore is subjected to continuous chemical and mechanical effect of a countercurrent flow of fresh gas, and the complete utilization of the gas is accomplished by adequate contact with fresh ore.

Large-scale Tests

The apparently satisfactory results obtained in the preliminary tests led to an attempt to apply the process in large-sized apparatus. Vertical, cylindrical retorts of cast Duralloy, having internal diameters of 3, 8 and 12 in., respectively, were constructed. These were (at different times) enclosed in a brick furnace having a heating zone about 4 ft. long. Provision was made for continuous feed and discharge of ore, but batch tests were also made. In some tests the gas passed upward through the ore (countercurrent), and in others the gas traveled downward and concurrent with the ore.

Difficulties Due to Reoxidation.—At first an attempt was made to prevent deposition of zinc oxide in the condenser or the flue connecting it with the retort by causing the reversal of reactions 3 and 4 to take place within the retort. To this end, the gas was passed upward through the ore, first through a reaction zone at 1000° C. and then through ore at temperatures as low as 800° C., before entering a flue leading to the condenser. The dew point for zinc is 783° C. in this process. At the lower temperature, reversal of reactions 3 and 4 deposits zinc oxide in the retort, and this zone was intended to prevent subsequent reoxidation and act as an intermediate condenser from which the trapped zinc oxide would travel downward with the ore and be redistilled. The plan was not successful, chiefly because the oxide deposit cemented the ore particles to each other and to the wall of the retort, producing a condition that impeded, and ultimately prevented, the flow of gas and movement of the ore. In other tests the gases left the retort at a high temperature, but deposition of zinc oxide in the flue connecting the condenser to the retort took place to such an extent that, no matter how large the flue, it was only a question of time (a day or two) until the passage was completely closed. It might be thought that this trouble could be overcome by removing the deposit at intervals, but this was found to be impossible, because the deposit is tough, hard, and adherent.

Summary of Results of Large-scale Tests.—The large-scale tests can only be described as premature. Their chief value was to delineate sharply, at an unjustifiable cost, the problems that were fundamental to any possible practical utilization of methane or natural gas for reducing zinc. In brief, the situation at the termination of 6 months of large-scale experimental effort was as follows:

1. Reoxidation due to side reactions 3 and 4 was shown to be a major practical difficulty.
2. The carbon formation, which had been minimized in small-scale tests, proved more troublesome on a large scale. Channeling of the gas stream, or contact of fresh gas with spent ore, inevitably results in excessive thermal decomposition of the hydrocarbons.
3. Cast alloy-steel retorts were proved to have an extensive life at temperatures not much above 1000° C., but their cost compared to equal capacity in a zinc-retort plant was excessive. Necessary fittings or connections could not readily be fabricated in the cast alloys.
4. When the retort was operated at low temperatures (925° to 950° C.), in order to minimize reoxidation difficulties, rates of zinc production somewhat less than that of an ordinary retort, based on volumetric displacement, were obtained. Such a rate would require for practical utility a retort of such large size as to imply serious problems of heat

transfer. At higher temperatures (1000° C.) the rate became, as has been indicated, several times that of a retort, but excessive reoxidation took place.

This effort was a failure because of chemical and mechanical difficulties, which adequately accounts for the fact that all previous attempts have also failed to develop a commercial process.

REOXIDATION

It was finally evident that unless reoxidation could be almost completely prevented, a continuous process would not be feasible, and for reasons to be discussed, batch operation is not satisfactory. In other words, the problem is essentially a chemical one and not amenable to a mechanical solution. With the object of preventing reoxidation, the reactions listed in Table 1 were intensively studied, thermodynamically and as to rates.

TABLE 1.—*Reactions Studied*

No.	Chemical Reactions	ΔH_{1323} (1050° C.), Cal.
1	$ZnO + CH_4 = Zn(gas) + CO + 2H_2$	105,900
2	$CH_4 = C + 2H_2$	22,040
3	$ZnO + CO = Zn(gas) + CO_2$	44,260
4	$ZnO + H_2 = Zn(gas) + H_2O$	51,765
5	$CO_2 + CH_4 = 2CO + 2H_2$	61,640
6	$H_2O + CH_4 = CO + 3H_2$	54,135
7	$CO_2 + C = 2CO$	39,600
8	$H_2O + C = CO + H_2$	32,095
9	$ZnO + C = Zn(gas) + CO$	83,860
10	$xZnO + yCH_4 = xZn + y(CO + CO_2) + 2y(H_2 + H_2O)$	

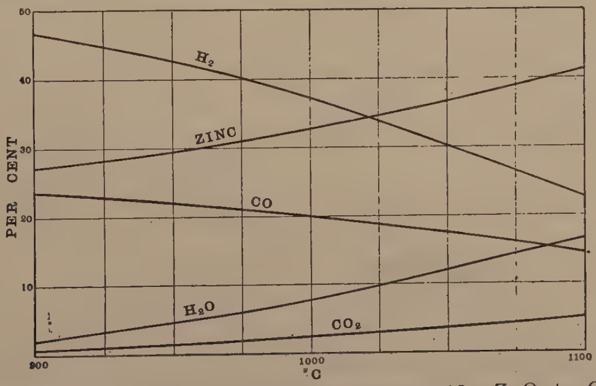


FIG. 1*a*.—EQUILIBRIUM CONCENTRATIONS FOR REACTION 10, $xZnO + yCH_4 = xZn + y(CO + CO_2) + 2y(H_2 + H_2O)$.

If methane is passed through a heated bed of zinc oxide at a slow enough rate, reactions 1, 3 and 4 reach an equilibrium that can be expressed by reaction 10 (Table 1). The equilibrium concentrations for the products of this reaction in the temperature range 900° to 1100° C. were calculated by applying the thermodynamic constants to the stoichiometric relations. The recent data by John Chipman[5] were used, and previously reported data have been recalculated on this basis. The results of these calculations are listed in Table 2 and shown graphically in Fig. 1. These data have major importance and experimental work has shown that they are substantially correct.

TABLE 2.—*Equilibrium Concentrations for Reaction* 10

	Concentration, Per Cent				
	900° C.	950° C.	1000° C.	1050° C.	1100° C.
Zn	27.1	29.5	32.7	36.7	41.2
CO	23.5	22.0	19.9	17.5	14.5
CO_2	0.8	1.5	2.6	3.6	5.1
H_2	46.6	42.5	37.1	30.2	22.6
H_2O	2.0	4.5	7.7	12.0	16.6

Reduced by	Percentage of Total Zinc				
Reaction 1	89.7	79.7	68.6	57.4	47.6
Reaction 3	2.9	5.1	7.8	9.9	12.2
Reaction 4	7.4	15.2	23.6	32.7	40.2
Reactions 3 and 4	10.3	20.3	31.4	42.6	52.4

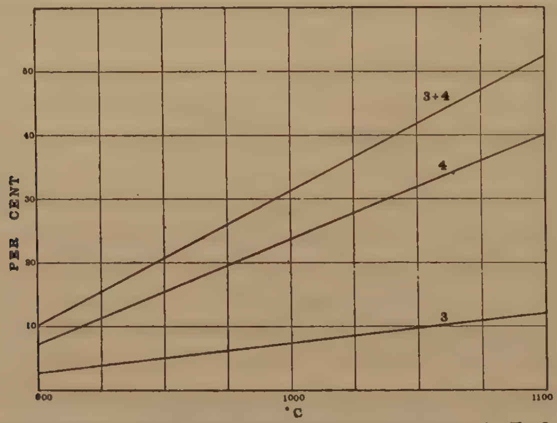


FIG. 1*b*.—PERCENTAGE OF TOTAL ZINC REDUCED BY REACTION 3, $ZnO + CO = Zn + CO_2$, AND REACTION 4, $ZnO + H_2 = Zn + H_2O$.

Reaction 1 is virtually complete in the temperature range indicated, and reactions 3 and 4 increase from negligible to large proportions as the temperature rises. Reaction 4 reduces two to three times as much zinc as reaction 3 and has a more rapid rate of reaction. (See Fig. 1*b*.)

These data cannot be obtained by direct analysis because when the gases are cooled reactions 3 and 4 reverse and change the composition of the gas. These secondary reactions and their reversals are shown by the reoxidation of zinc that occurs, and they have been tested quantitatively by passing CO or H_2 through a heated bed of zinc oxide. The reversal of reaction 4 is so rapid and complete that H_2O has not been found in the products of reaction 10, although the CO_2 content is usually about 50 per cent of the equilibrium quantity.

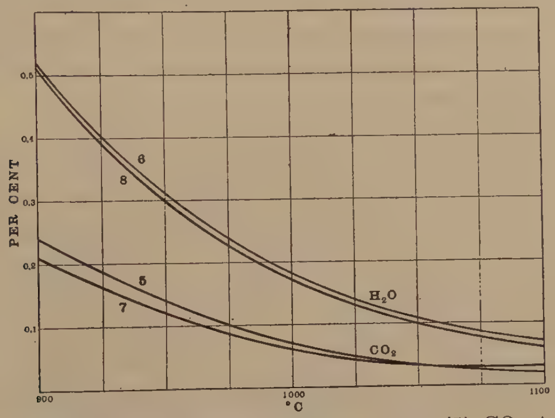


FIG. 2.—EQUILIBRIUM CONCENTRATIONS FOR REACTIONS: (5) $CO_2 + CH_4 = 2CO + 2H_2$; (6) $H_2O + CH_4 = CO + 3H_2$; (7) $CO_2 + C = 2CO$; (8) $H_2O + C = CO + H_2$.

The amount of zinc reduced by reactions 3 and 4 in terms of total zinc reacting is shown in Fig. 1*b*. Since reversal of 4 is complete and of 3 about 50 per cent complete during the time required to condense the zinc, about 9, 27 and 46 per cent of the total zinc distilled at 900°, 1000° and 1100° C., respectively, will be reoxidized.

Secondary Reactions

Reactions 5, 6, 7 and 8 provide means by which reoxidation can be prevented. The equilibrium constants of these reactions were calculated for the temperatures 900°, 1000° and 1100° C. It was then assumed that the equilibrium products of reaction 10 reached a second equilibrium with CH_4 and C, respectively, keeping the gas pressure constant at 1 atmosphere. Applying the thermodynamic constants to the stoichiometric relations involved gave the results listed in Table 3. The CO_2 and H_2O concentrations are plotted in Fig. 2.

The equilibria above 1000° C. for these reactions reduce the concentrations of CO_2 and H_2O below 0.1 and 0.2 per cent, which is not enough to cause reoxidation of zinc.

The composition of the gas resulting from the reactions of methane with the products of reaction 10 is the same as that obtained by reaction 1. This is a necessary consequence of the fact that the algebraic sums, or net results of equations 3 plus 5 or 4 plus 6 are identical to the primary reaction 1. From this it follows that the side reactions do not affect the amount of zinc produced by a unit quantity of methane. But, since the side reactions take place before reaction 1 is completed, they give an apparent rate for reaction 1 that is greater than its true rate. If the reactions are not given time to reach equilibrium, they will give a product having a composition intermediate between the equilibrium concentrations listed in Table 2 and those for reactions 5 and 6 in Table 3.

The composition of the gas resulting from the reactions with carbon (Table 3) is considerably different, because the ratio of CO to H_2 is increased by substituting carbon.

TABLE 3.—*Equilibrium Concentrations for Secondary Reactions on Products of Reaction* 10

		Concentration, Per Cent		
		900° C.	1000° C.	1100° C.
Reactions 5 and 6	Zn	25.57	25.18	25.07
	CO	24.57	24.88	24.96
	CO_2	0.24	0.06	0.02
	H_2	49.10	49.70	49.88
	H_2O	0.52	0.18	0.07
Reactions 7 and 8 (with carbon)	Zn	26.54	29.76	33.92
	CO	25.61	29.45	33.80
	CO_2	0.21	0.07	0.03
	H_2	47.13	40.55	32.19
	H_2O	0.51	0.17	0.06

The normal rates of these reactions are too low to have practical use. No method of catalyzing the reactions with carbon has been found. The methane reactions, however, can be enormously accelerated by means of nickel catalyst.

Catalytic Reaction Rates

The catalyst may be prepared by wetting alundum granules (−4 mesh to a +8 mesh) with a saturated solution of nickel nitrate and heating the dried product to 600° C. The size of the granules, the size and *shape* of the catalyst chamber, the temperature, the composition of the gas mixture, and its rate of flow all determine how rapidly and completely the catalyzed reactions will proceed.

Fig. 3 is a plot of data relating to the rates of reactions 5 and 7. To obtain curve *A*, CO_2 was passed through a bed of coke (¾ in. in diameter by 9 in. long), composed of −4 +8-mesh grains heated to 1000° C. The gaseous products were analyzed, and the ratio $CO_2/CO + CO_2$ (ordinate) was plotted against the rate of flow (abscissa). Curves *B* and *C* are from similar data, obtained by passing an equimolal mixture of CO_2 and CH_4 through a bed of nickel catalyst at 1000° C. In each instance the abscissa represents liters per hour of CO_2 only. In *B*, the bed of the catalyst measured ¾ in. in diameter by 3 in. in length. In *C*, the same sample of catalyst was in a bed ½ in. in diameter by 6 in. long.

It is at once evident that the carbon reaction is much slower than the catalyzed reaction. Unless catalyzed, however, reaction 5 is even slower than the carbon reaction. Comparison of curves *B* and *C* shows that the reaction is more complete after passing through a long column of small cross section than after passing through the same amount of catalyst with less length and a larger cross section. The sharp break in curves *B* and *C* shows that the catalytic capacity has a very sharp limit. At rates of flow above this limit carbon is deposited, impairing the effectiveness of the catalyst. At temperatures below 1000° C. the reaction rate drops rapidly with decreasing temperature.

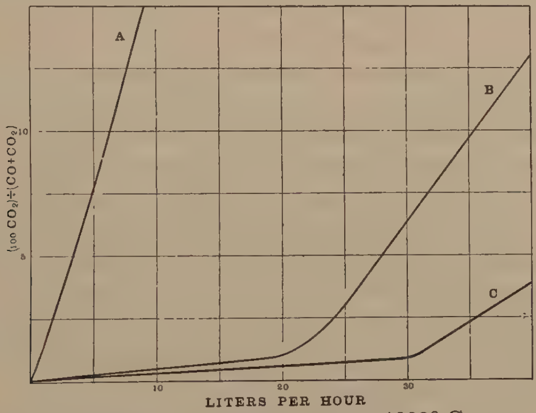


FIG. 3.—REACTION RATES AT 1000° C.
A = reaction 7, *B* = reaction 5 (catalyzed by 3-in. column), *C* = reaction 5 (catalyzed by 6-in. column).

Reaction 6 also is catalyzed. No data on the rate of this reaction were obtained, but it is probably even faster than reaction 5.

There was at first some doubt as to how zinc vapor would affect the catalyst. In tests to determine this point, it was found that a small amount of zinc became alloyed with the nickel. This action decreased the rate of the catalytic reactions only slightly.

Obviously, the catalyzed reactions must take place *after* the gases have left the ore, otherwise CO and H_2 would again react with ZnO and defeat the purpose of this step. Moreover, the gases must contain enough CH_4 to react with all the CO_2 and H_2O present; but if there is a large excess of CH_4, carbon will be deposited because reaction 1 is also catalyzed. Since a drop in temperature causes a reversal of reactions 3 and 4, the catalysis must take place *before* the temperature of the gas is lowered. An increase in temperature is preferable, because it will increase reaction rates and decrease equilibrium concentrations of CO_2 and H_2O.

If methane is passed through a heated bed of zinc oxide at such a rate that reaction 1 does not attain equilibrium, the gaseous products will contain methane. The rate of flow may be regulated so that the excess methane just suffices to satisfy the requirements of reactions 5 and 6. Under these conditions reactions 3 and 4 in the retort, plus reactions 5 and 6 during the catalysis, will give a net result equal to reaction 1, and the gaseous products will have the same composition as those produced by reaction 1.

The rate at which reaction 10 occurs increases rapidly when the temperature is raised, but the concentrations of CO_2 and H_2O likewise increase. Unless the latter are removed before the zinc is condensed, commercial application of the reaction would be limited to low temperatures and low reaction rates, and even then reoxidation causes serious difficulties. By the use of catalyzed reactions 5 and 6, not only may high temperature and high reaction rates be utilized, but reoxidation is virtually eliminated, and the side reactions contribute a large share of the zinc recovered as metal. The net result is a rate of zinc production per unit volume of retort space several times as large as that obtained in the usual commercial practice.

It is neither feasible nor necessary to measure the relative rates of all the reactions under comparable conditions as was done for reactions 5 and 7. A rough comparison of the rates at 1000° C. under the conditions in which they react in the process, however, may clarify the situation.

Reaction 1 is moderately rapid and at equilibrium substantially complete. Under operating conditions the rate of gas flow is sufficiently rapid so that considerable CH_4 (enough to react with all the CO_2 and H_2O from reactions 3 and 4) passes through the retort without reacting. We will arbitrarily call this rate 100.

Reaction 2, in the presence of zinc oxide, is so much slower than reaction 1 that its effect at 1000° is small. This rate is estimated to be in the order of magnitude 1, as compared to reaction 1. As the gas enters the reaction zone, considerable carbon is deposited in the temperature range 600° to 900° C. Most of this carbon comes not from CH_4 but from the higher members of the methane series present in the natural gas.

Reactions 3 and 4 are so much faster than reaction 1 that they practically reach equilibrium as fast as they are formed by that reaction. We can assume therefore that the equilibrium values of reaction 10 apply to all the methane that reacts. The relative rates are estimated at 500 and 1000 for 3 and 4 respectively, as compared with reaction 1.

Reactions 5 and 6 are normally very slow and their effect in the retort is negligible. When stimulated by the nickel catalyst they are very rapid. Normal rates for 5 and 6 are estimated as 1 and 2, respectively, catalyzed rates as 200 and 400.

Reactions 7 and 8 are much slower than reaction 1. They are estimated at 10 and 20, respectively.

Reaction 9 is the sum of reactions 3 and 7 or of reactions 4 and 8. Whatever the mechanism may be, it is not faster than the slower step of the component reactions 7 and 8, the rates of which are estimated at 10 and 20, respectively.

Thermal Requirements

The last column in the list of reactions is ΔH_{1323}; or the heat required by the reactions at 1050° C. in calories per gram-mole involved. Note that reactions $3 + 5 = 4 + 6 = 9 + 2 = 1$. Also reactions $3 + 7 = 4 + 8 = 9$. These relations apply to the stoichiometric results and also to the thermal requirements. Therefore 105,900 cal. of heat must be supplied to reduce one mole of zinc with methane and 83,860 to reduce it with carbon, regardless of the intermediate steps involved. The difference between the two is the heat of formation of methane (reaction 2, or 22,040 cal.).

From the equilibrium concentrations at 1050° C. (Table 2) we find that reaction 1 reduces 57.4 per cent of the zinc, reaction 3 reduces 9.9 per cent and reaction 4 reduces 32.7 per cent. Each mole of zinc, therefore, requires

$$(0.574 \times 105{,}900 + 0.099 \times 44{,}260 + 0.327 \times 51{,}765) = 82{,}100 \text{ cal.}$$

for reaction 10. The remaining 23,800 cal. must be supplied to catalytic reactions 5 and 6. Since the latent heat of combustion in the gaseous products of these reactions ($CO + 2H_2$) is 183,430 cal., the extra heat required for gaseous reduction is unimportant.

THERMAL DECOMPOSITION

The city gas supply at Berkeley contains about 86.85 per cent CH_4, 7.86 per cent C_2H_6, 3.87 per cent C_3H_8 and smaller amounts of the higher homologues. The reducing power by reactions analogous to reaction 1 is proportional to the carbon content, which in this gas is about 20 per cent higher than that of methane. On the other hand, the homologues are less stable than methane and decompose more readily into carbon and hydrogen. Under the experimental conditions used in this investigation, about half the reducing power of the higher members is *directly* utilized.

In a retort with continuous feed and discharge of ore, the carbon deposited by thermal decomposition of the gas moves with the ore into the high-temperature zone and is utilized more or less by reactions 7 and 8, which, when supplemented by reactions 3 and 4, give a result identical to that of reaction 9. That this is the mechanism mainly responsible for the reduction of zinc oxide by carbon, even in the usual retort practice, has been previously shown[2]. As a result of these reactions the effective reducing power of natural gas may be higher than that of methane.

The homologues of methane in natural gas, their thermal decomposition by reaction 1, and the compensating effect of reactions 7 and 8 produce variations in the composition of the gaseous products, so that the ratio of CO to H_2 in the exit gas may vary considerably from the theoretical (1 to 2) by reaction 1.

Thermal decomposition of the gas, under certain conditions, causes low utilization of the gas and also mechanical difficulties as a result of carbon deposits. Below 870° C. reaction 2 takes place in preference to reaction 1. Above 900° C., in the presence of an adequate surface of zinc oxide, there is no appreciable deposition of carbon, although almost any other surface catalyzes reaction 2 and the rate of that reaction increases with increasing temperature.

If the ore and gas are passed countercurrently through a retort for some time, so that the gas first contacts lean ore residues, a large portion of the gas will be thermally decomposed before it has an opportunity to react with zinc oxide. In a batch process the same situation arises before a high extraction of the zinc is accomplished. Therefore, a concurrent travel of ore and gas is necessary, and a batch process cannot be efficient.

On the other hand, concurrent operation alone does not permit a high utilization of the gas and at the same time give a high extraction of the zinc content of the ore. This might be possible if it were not for the requirement of the catalytic reactions which demands an excess of CH_4 in the offtake gas. The difficulty was solved by using a concurrent flow of gas and ore in the upper half of the retort and a countercurrent flow of a portion of the condenser exit gas ($CO + H_2$) in the lower half of the retort. The two streams of gas meet at an offtake flue at the center of the retort.

The concurrent flow of "primary" gas extracts about 80 per cent of the zinc and produces about a 75 per cent decrease in the volume of the ore. Therefore, the rate of travel (of solids) through the lower part of the retort is about one-fourth the rate at which ore is charged. This relatively slow travel permits a very high extraction of the zinc from the unfused residues by the action of the countercurrent flow of recirculated exit gas. Since this gas is a mixture of CO and H_2, it will not deposit carbon. In fact, carbon that has been deposited by the primary gas and descended with the ore is to some extent utilized by means of reactions 7 and 8.

Incidentally, the countercurrent flow of gas prevents diffusion and condensation of zinc vapor into the cold zone through which residues are discharged.*

EXPERIMENTAL APPARATUS

The laboratory apparatus used to test the revised process was designed not only to test the chemical reactions in a continuous operation but also to serve as a small model of a feasible commercial unit, using materials of construction that are suitable and available for large-scale equipment. It was large enough so that the quantitative results and operating technique can be utilized in the development of larger units.

The primary requirements of the retort and catalyst chamber are that they be gastight and constructed of material capable of resisting chemical action at the high temperature. The chromium-iron alloys are the only satisfactory materials found for this service. Alloy castings can be used, but the sheet metal can be shaped and welded into the required form at much lower cost than castings. The sheet-metal retort also has thinner walls and offers less resistance to the transfer of heat.

Refractory materials are most suitable for the condenser. During most of the experimental work molded alundum units were used. Porcelain, with an inside glaze, was finally tested and found to be greatly superior.

In a previous publication[6] the essential features of an early form of an experimental furnace are shown. The details of design evolved, through many changes, to the final form illustrated in Figs. 4 and 5. Fig. 6 is a photograph of the retort, catalyst chamber and condenser; Figs. 7 and 8 are two views of the complete furnace.

Description of Retort

Fig. 4 shows a section of the apparatus through the vertical axes of the retort and condenser. A Nelson pump (1) is connected by reduction gears to ⅙-hp. motor 35. Gas from the city main is drawn through a gas meter (not shown) into the pump, which delivers it through flowmeter

---

* The marked advantages accruing through recirculation of exit gas suggests the use of a system in which zinc is extracted from the ore by a countercurrent flow of exit gas, the methane or natural gas being used only for the catalytic reactions. One difficulty of such a plan would be the problem of admitting exactly the proper proportion of natural gas at a point between the retort and catalyst chamber and preventing obstruction of this gas inlet by the inevitable deposition of carbon. Moreover, the amount of primary gas per pound of zinc extracted would not be affected because the reactions $3 + 5 = 4 + 6 = 1$. It so happens that 1 mole of CO and 2 moles of H_2 in equilibrium at 1050° C. react with about 1 mole of zinc. These reactions require 49,400 cal. Then, 1 mole of CH_4 and 56,500 cal. must be supplied for the catalytic reactions, and the zinc vapor is thus diluted by twice as much gas as when zinc is extracted by reaction 10. Thus substitution of exit gas for methane would double the work required of the catalyst and condenser.

2 and tube 3 to ore hopper 4. The latter is a short 2-in. pipe, with each end threaded to a 2 by 1-in. pipe reducer. The upper end is closed by a plug and the lower end threaded to the upper end of retort 5. The retort is constructed of 10-gauge Ascalloy, and all joints are gas-welded. The upper end is a 1-in. pipe joined by a cone to a 3-in. pipe. The latter is joined and projects into the lower half of retort 19, which consists of a short 4-in. pipe and a short 2-in. pipe joined by a cone. A horizontal

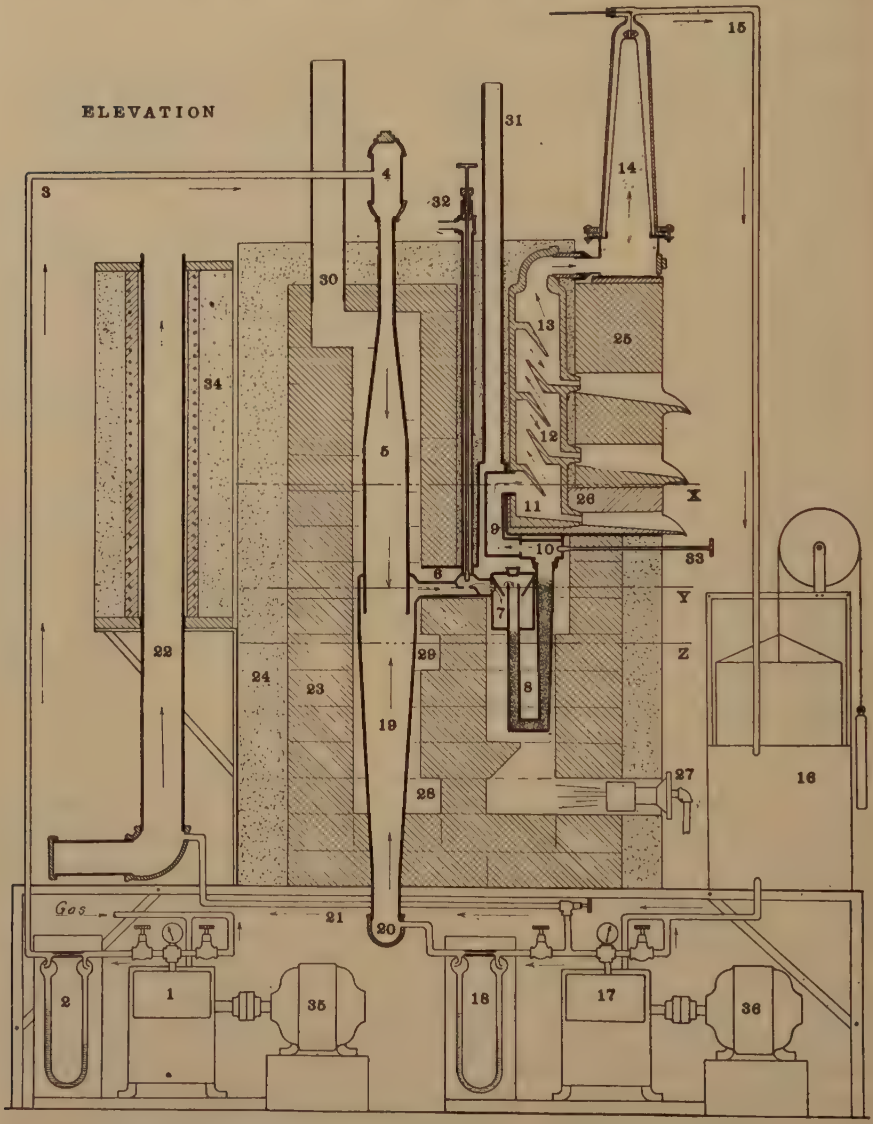


Fig. 4.—Sectional elevation of laboratory zinc furnace.

1-in. ore-discharge pipe is connected to the lower end of the retort by a 2 by 1-in. bushing and 2-in. elbow 20.

Extending horizontally from the annular space formed by the extension of the upper 3-in. section of the retort into the lower 4-in. section is a short flue provided with a special alloy globe valve 6, which connects the retort to the cyclone-type dust collector 7, also constructed of alloy. Extending into and from the axis of the dust trap is U-shaped catalyst tube 8, the second leg of which is joined removably by a tapered fit into valve chamber 10. A C-shaped alloy flue 9 connects valve 10 with lower condenser chamber 11. An alloy partition and stack 31 make it possible to control the temperature of flue 9. All cross sections of the sheet alloy are indicated by double-width solid lines.

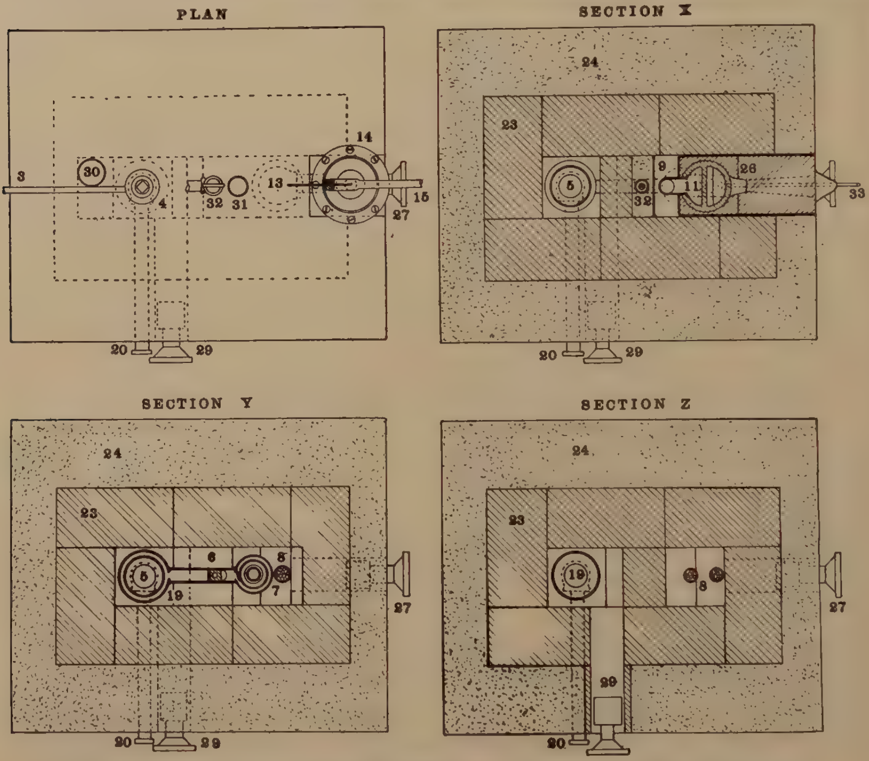
Valves 6 and 10 are two-way valves of unusual construction. Valve stems 32 and 33 terminate in pear-shaped plugs, which in the position shown make a gastight fit in the tapered hole through which the valve stem enters the valve chamber. When the valve stems are pushed inward the plugs fit snugly in the tapered valve seats, and the stems fit loosely. In this way the catalyst chamber is sealed off from the retort and the condenser and at the same time is provided with an external gas inlet 32 and outlet (past stem 33). These valves are not difficult to construct and operate with entire success at temperatures as high as 1050° C.

A tapered plug closes a hole in the top of dust trap 7. A film of waterglass gives a gastight seal at this joint, as well as that under valve 10.

Condensers 11, 12 and 13 form a monolithic cylinder of alundum or porcelain (3 in. in internal diameter) with partitions for deflecting the gas flow and providing traps for condensed metal. Tapping spouts project from the three metal traps into conical outlets in fire-clay insulating blocks 25 and 26. Block 26 forms a base for the condenser. It is molded in place and seals the joint between flue 9 and the first condenser chamber 11. The condenser is made in seven sections (each one except the top having one partition) by tamping moist alundum cement into a split mold. These sections are trimmed and joined together while still "green," and the top section is capped by an elbow of the same material, which connects with a short alundum pipe leading to bag filter 14. The latter is a cylindrical iron base with inlet and capped outlet ports on opposite sides, a flat bottom plate, and a top flange having an inner ring to which a wool bag is fastened. Encasing the bag and clamped to the base flange is a glass bell; the clamped joint is made gastight by a rubber washer. A glass T at the top of the bell provides a gas outlet to tube 15 and a seat for the rubber stopper, through which is inserted a shaking rod to support the bag.

A storage tank 16 for the exit gas is connected to pump 17, the outlet of which has two valve-controlled branches, one leading through a flowmeter to the bottom of the retort and the other to ore pretreatment furnace 22. The latter is a vertical, 3-in., iron pipe, connected at the bottom by an elbow to a short, capped, ore-discharge pipe. The upper end is encircled by an insulated heating element 34.

The alloy retort, catalyst chamber, and connecting flues are enclosed in firebrick chamber 23 and insulated by Sil-O-Cel 24, which is held by a sheet-metal casing. The retort and catalyst are heated separately by gas burners through ports 28, 29 and 27. The heating gases exit by flues 30 and 31. The whole furnace structure rests upon a metal plate supported by an angle-iron frame.



PLAN

SECTION X

SECTION Y

SECTION Z

FIG. 5.—PLAN AND HORIZONTAL SECTIONS OF LABORATORY ZINC FURNACE.

Fig. 5 shows a plan and horizontal sections of the furnace at planes *X*, *Y* and *Z* indicated on Fig. 4.

Accessories not shown in the illustration include pyrometers, pressure gauges and gas meters.

The catalyst is finely divided nickel on an alundum base, prepared from grains of alundum which pass a 4-mesh screen and are retained on an 8-mesh screen. These are wet with a saturated solution of nickel nitrate, dried, and then heated to a red heat. At or above this temperature the nickel oxide is reduced by a stream of hydrogen.

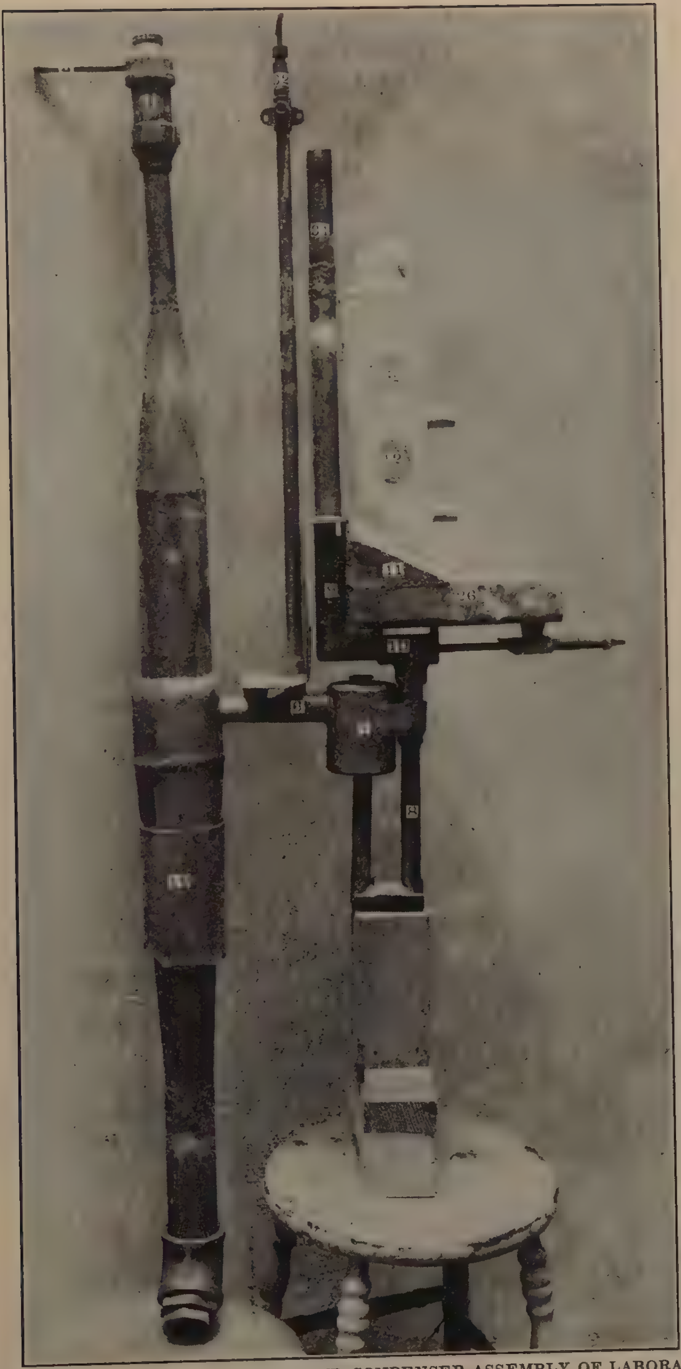


FIG. 6.—RETORT, CATALYST CHAMBER AND CONDENSER ASSEMBLY OF LABORATORY ZINC FURNACE.

Operating Procedure

By means of gas burners 27, 28 and 29 the furnace is heated to the temperatures shown in Fig. 9. The retort is nearly filled with partly treated ore from a previous run and the charge completed with fresh calcine from pretreater 22. The cold ore reaches the furnace temperature in a few minutes, and a flow of gas (about 50 liters per hour) is then pumped into the retort through line 3. To prevent contamination of the stored exit gas with nitrogen, line 15 is disconnected the first 20 min., the exit gas being vented through a restricted opening to maintain low pressure in the condenser. At the same time, exit gas (stored in 16 from a previous run) is pumped through meter 18 into the lower end of the retort at 20, also at a rate of about 50 liters per hour. At first most

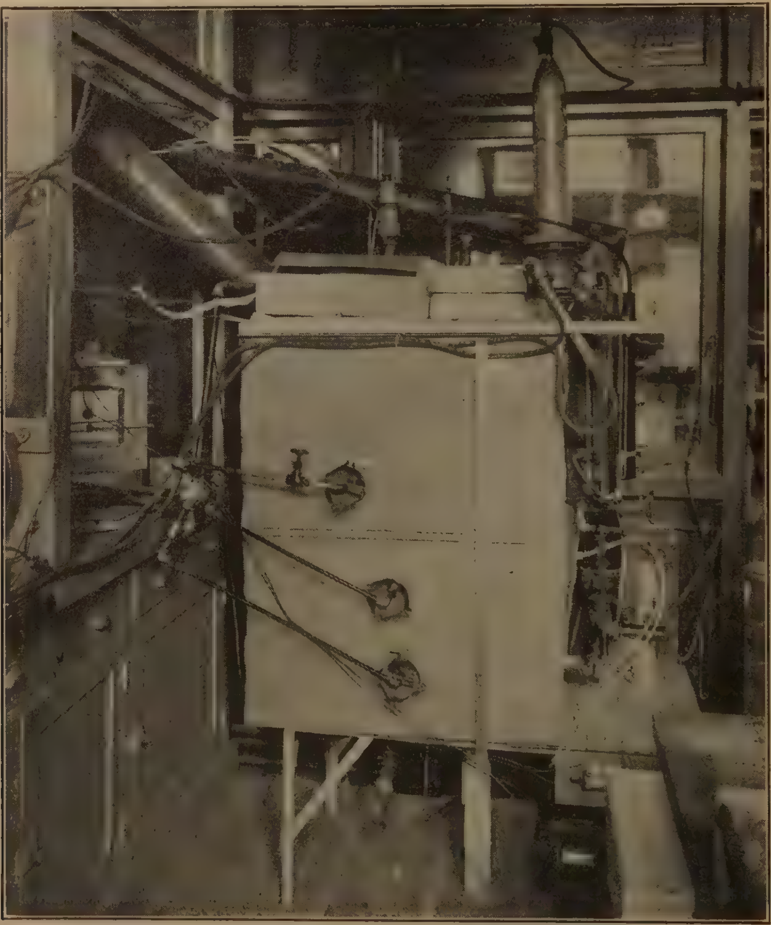


Fig. 7.—Side view of laboratory zinc furnace.

of the gases diffuse through the pores and joints of the condenser, but these gradually become sealed with metal and zinc oxide. (The tapping spouts are sealed with asbestos fiber and fire-clay mud.) After operating a few hours there is very little leakage from a well made condenser.

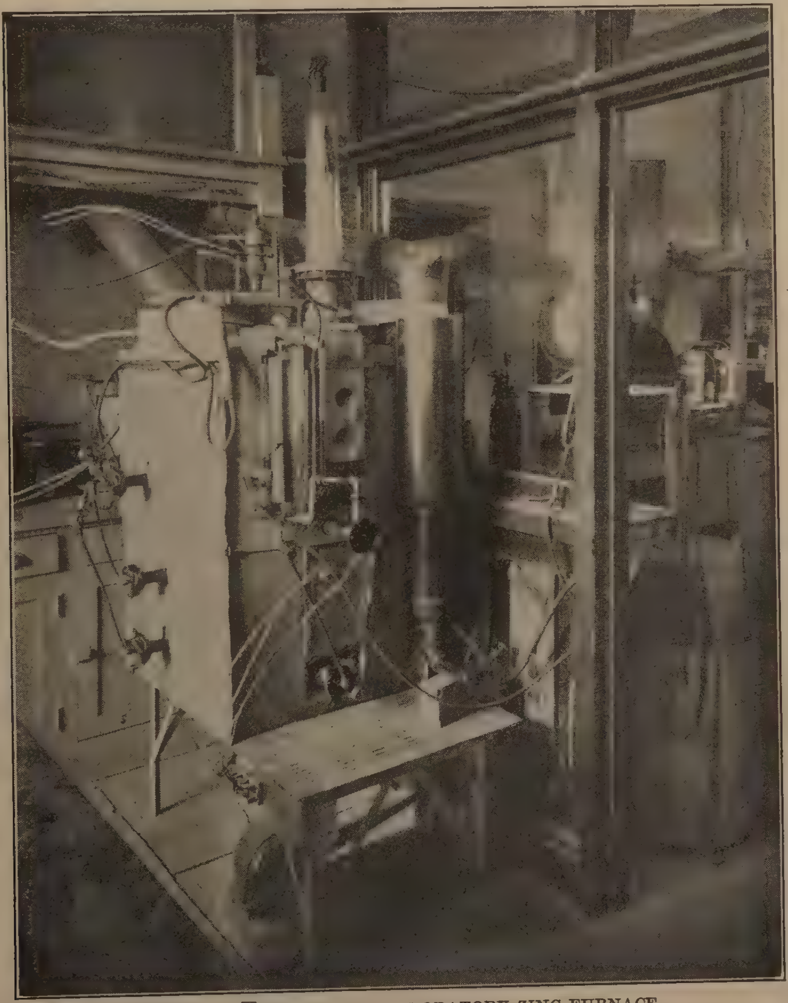


FIG. 8.—END VIEW OF LABORATORY ZINC FURNACE.

As stated, after 20 min. of operation line 15 is connected to gas tank 16, the balance weight being adjusted to give a back pressure of 1 in. of water. At the same time, the valve leading to line 21 and the pretreatment retort is opened just enough to discharge gas as fast as it accumulates. An electric buzzer, operated by contacts placed on the wheel over which the balance weight of the gas receiver is hung, gives warning that the valve requires adjustment. In a more elaborate setup, regulation could well be made automatic.

At 2-hr. intervals ore is charged and residues discharged. To do this the flow of gas must be interrupted about 5 min. The cap on the ore-discharge pipe (see plan view 20) is removed, a conveyor screw is inserted, and about 80 grams of residue is drawn off. After this opening is closed the cap on the ore hopper is removed, the charge is rodded slightly with a heavy wire, and the hopper is filled with ore and capped. The gas pumps are then started at once, and normal operation is resumed.

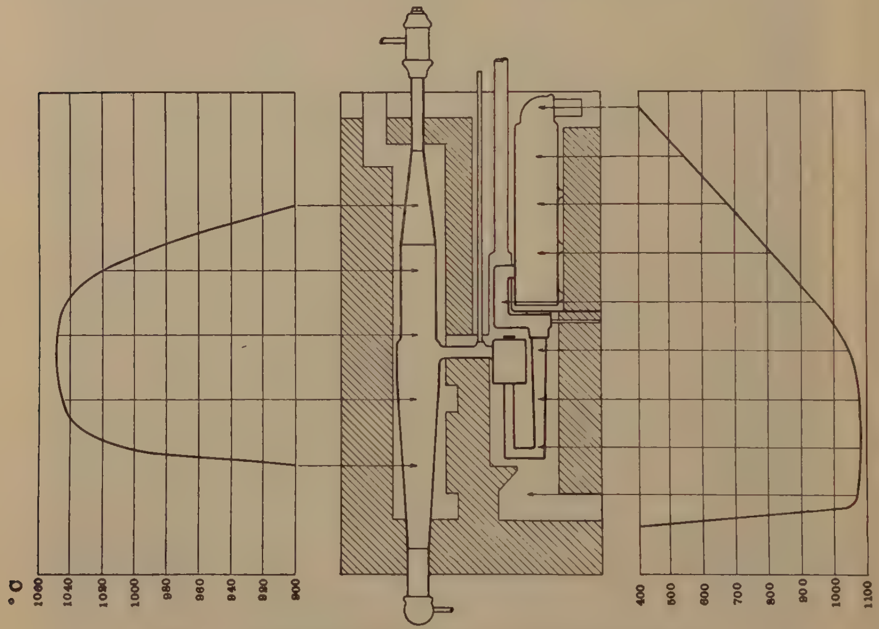


FIG. 9.—TEMPERATURE CHART OF THE ZINC FURNACE.

Charge and discharge weights are recorded; then all temperature, gas-meter, flowmeter and pressure-gauge data are taken. Next, a sample of exit gas from a branch in line 15 is drawn off and analyzed for CO_2, CO, CH_4 and H_2. The CH_4 content should be between 0.1 and 1.0 per cent and is controlled by the rate of gas input. If too high, the efficiency of gas utilization is impaired, and an excessive amount of carbon is deposited on the catalyst. If too low, zinc will reoxidize in the condenser. The latter condition is determined infallibly by the CO_2 content of the exit gas, which should not be more than 0.2 per cent. If the catalyst is functioning properly and the slightest excess of CH_4 is present in the exit gas the CO_2 content will be low.

Usually, after about 50 hr. of operation, the activity of the catalyst is impaired, and it must be regenerated. This is accomplished by stopping the flow of gas through the retort, closing valves 6 and 10, and passing a stream of hydrogen and then CO_2 alternately into inlet 32 for a total period of 30 to 60 min. These gases pass through the catalyst and exit past valve stem 33 into the combustion chamber. Sometimes it is necessary to regenerate the catalyst, not on account of low activity but because deposition of carbon in it has increased its resistance to the flow of gas beyond a satisfactory working limit.

Criteria for Control of Operations

Temperature.—The capacity of the furnace increases with the temperature, therefore the latter is maintained as high as the retort metal will resist, or about 1050° C. maximum, allowing a small factor of safety against fluctuations.

Rate of Gas Input.—Gas should be supplied at a rate that will yield a final gas product (exit gas) containing 0.1 per cent of methane. If the temperature does not vary and if a uniform rate of charging the ore and discharging residues is maintained for a long period, a constant rate of gas flow will give uniform results. A change in temperature or in the composition of the retort charge will require a compensating change in the rate of gas input.

Rate of Charging Ore.—After the proper rate of gas flow has been determined and maintained several hours, the reduction rate is calculated from the CO content of the exit gas. Each mole of CO corresponds to one mole of zinc extracted from the ore. From these data the proper rate of charging ore and discharging residues can be calculated for any degree of extraction required. The ore is charged as rapidly as the reduction of volume in the content of the retort permits, and its rate is actually determined by the rate at which residues are removed. If these are discharged too rapidly they will have a high zinc content, but it is feasible to re-treat a limited portion of such residues.

The CO/H_2 ratio in the exit gas also indicates the condition of the ore charge. If temperatures and rate of gas flow are constant a decrease in that ratio results from a decrease in the zinc content of the charge, and vice versa. This follows from the fact that a deficiency of zinc oxide retards the rate of reaction 1 and the relative effect of reaction 2 increases. The zinc extracted during the 2 hr. between charging periods has a noticeable effect upon the CO/H_2 ratio.

Good results can be obtained, even with considerable variation in temperature and rate of ore and gas input, but a close control of these factors is very much to be desired. A change of 10° C. has a marked effect upon reaction rates and upsets the balance between the rates of gas and ore input. This changes the ratio of methane to CO_2 and H_2O in the gas leaving the retort, and the proper ratio is essential for the catalytic reactions.

Manual vs. Automatic Regulation

With manual control of operations alertness and experience are required to maintain even approximately uniform conditions. Temperature control was most difficult because of fluctuations in the pressure of the gas used for heating and the lag between a change in adjustment of a burner and the pyrometric effect. For this reason, quantitative data on the effect of small variations in rates of gas and ore input, temperature, etc., have not been obtained.

There is good reason to believe that maintenance of uniform operating conditions, which can be accomplished by means of automatic devices, would aid in determining and preventing conditions that sometimes cause inefficient catalysis.

Catalytic Poisoning and Regeneration

One cause of poor catalysis—deposition of carbon—can be prevented by close control of temperature and rate of gas input. Poisoning from sulphur compounds can be more or less completely prevented by: (1) maintaining the temperature as much higher than that of the retort as is feasible; (2) more complete elimination of sulphur by pretreatment of the ore; (3) reducing the temperature of the retort; (4) reducing the amount of gas recirculated.

Deposition of Carbon

The sharp taper in the upper end of the retort was designed to increase the velocity of gas flow and thus reduce the time during which the gas passes through the temperature range of thermal decomposition (about 500° to 900° C.). By this means, deposition of carbon was limited to not more than half the carbon content of the higher members of the methane series present in the natural gas. If pure methane were used instead of natural gas the deposition of carbon would be negligible.

The carbon that was deposited caused no mechanical difficulties. In some tests small amounts of crushed coke were added to the ore in order to reduce the sintering of residues due to exceptionally high metallic iron content of those residues.

The amount of carbon formed by thermal decomposition could not be accurately determined because, during its travel through the retort, and especially in the recirculation zone, it reacts according to equations 7 and 8. The amount of carbon in the residue is thus a net result of equations 2, 7 and 8.

Recirculation of Gas

It was not possible in this apparatus to maintain the temperatures, rates of ore charged and rates of gas flow with sufficient precision so that significant data concerning the effect of variation in the proportion of exit gas recirculated could be obtained. About one-third of the exit gas (a volume equal to that of the primary gas used) was recirculated, and no definite effect from a considerable variation of that rate could be detected. An increase in the proportion of exit gas should increase the capacity of the retort and increase the amount of work required of the catalyst. The latter effect could be noted by the increase of CO_2 in the exit gas when the proportion recirculated was excessive.

Condensation

The condensation of zinc from the products of reduction with natural gas presents problems and difficulties not encountered in present practice. First, more condensing surface is required because of the much lower concentration of zinc vapor in the gas. After reduction with carbon the zinc concentration is approximately 50 per cent, a dilution of 1 to 1. With natural gas the maximum concentration is 25 per cent, a dilution of 4 to 1. However, with adequate condensing surface at the proper temperatures condensation is practically complete.

The practical necessity of recovering the gaseous products for further use and the large condensing surface required have led to development of a more elaborate and expensive condenser than usual practice dictates. The advantages of the new form are as follows: (1) practically complete recovery of the metal; (2) condensation in stages, separating the metal into different grades of exceptional quality; (3) continuous operation; (4) recovery of gaseous products.

The disadvantages are: (1) high initial cost; (2) inaccessible passages, which cannot be mechanically cleaned out when fouled.

Long life for such a condenser is thus a practical necessity. To prevent rapid fouling of the condenser and to devise a workable method of cleaning a fouled condenser have been *major* problems of this work.

Solution of the problems has been slow because several distinct and unrelated factors cause the reoxidation mainly responsible for fouling. These factors are:

1. Reversal of reactions 3 and 4. By the catalytic reactions, reoxidation from this source has been reduced to a negligible amount.

2. Interruptions in the flow of gas during the charging of ore, etc., cause reoxidation because the excess CH_4 (required for the catalyzed reactions 5 and 6) is eliminated by reaction with ore and when the flow of gas is resumed the CO_2 and H_2O content (nearly at equilibrium concentrations) pass unchanged through the catalyst and produce reoxidation in the condenser. Automatic feed and discharge of the ore will overcome this difficulty.

3. Reoxidation from CO_2 produced in the condenser by reversal of reaction 7; i.e., $2CO \rightarrow C + CO_2$. At the temperature of the condenser the reaction rate is negligible unless catalyzed. A porous refractory, such as alundum, has a catalytic action, and even traces of iron have a marked effect. Trouble from this source has been completely avoided by the use of a glazed porcelain condenser.

4. Reoxidation by air that diffuses through cracks and porous walls of the condenser. At the temperatures of condensation the rate of diffusion through the wall of a well made alundum condenser is surprisingly high. This diffusion takes place even if the gas pressure inside is considerably above atmospheric. After the condenser walls have become coated with metal this source of oxidation is greatly reduced but not entirely prevented. The porcelain condenser overcame this source of trouble and revealed that the porous refractory material previously used was the chief cause of reoxidation.

When a run is started with a new alundum condenser, the exit gas may contain as much as 10 per cent nitrogen and 2 per cent CO_2. These constituents gradually decrease, and after 5 to 10 hr. operation the composition of the exit gas is normal. As a result of the large amount of reoxidation in the condenser during such a start it becomes so fouled after 100 or 200 hr. of operation that gas can no longer pass through it.

In the first run with a porcelain condenser inspection of the contents after 168 hr. of operation revealed only a small quantity of oxide. It was estimated that at least 400 hr. of such service would be feasible. In a larger unit, with larger condenser passages and more precise control of operating conditions, the condenser should give uninterrupted service for 30 days, possibly very much longer.

The cost of a shutdown and replacement of the condenser even at such intervals would be a considerable item, which can be avoided by providing two condensing systems for each retort. By the use of alloy valves (the satisfactory functioning of which has been amply demonstrated), either condenser can be blocked off while the other is in use. When a condenser becomes fouled the valves can be reversed, so that the fouled unit can be cleaned while the other is in use. A condenser can be cleaned completely by heating it to 1000° C. with auxiliary burners and passing exit gas through it. The fumes thus produced can be burned and the zinc oxide recovered in a bag filter.

It is also quite feasible to construct a separate catalyst chamber for each condenser and thereby enable "poisoned" catalyst to be regenerated without interrupting operation of the retort. Details of a design for a large unit with two catalyst chambers and two condensers will be discussed later.

The condensed metal collects in condenser traps 11, 12 and 13 (Fig. 4). Most of the lead collects in the lower trap 11, about two-thirds of the zinc in 12, and most of the remaining zinc in 13. The lead content of samples from a furnace run during 100 hr. of operation are as follows: (No. 11) 56.1 per cent Pb, (No. 12) 0.052 per cent Pb, (No. 13) 0.023 per cent Pb. Cadmium could not be detected by wet methods of analysis in any of these products, probably because of its efficient removal in the pretreatment process.

The concentration of zinc vapor in the gas entering the condenser is about 25 per cent. The dew point at that concentration is about 785° C. The temperature in the lower part of the condenser (trap 11) should be held at 800° C. to condense most of the lead and but little zinc. There should be a gradual drop in temperature as the gases travel upward, and the condenser outlet should be above 419.4° C., the melting point of zinc. At 450° C. the vapor pressure is 0.18 per cent of the pressure at which zinc enters the condenser.

Since only 0.3 per cent of the zinc passed through the condenser, as determined by that caught in the bag filter, condensation was as good as could be expected. The filter was installed to prevent clogging of the valves in the gas-recirculation system. These valves were barely "cracked" and even a minute amount of dust affected their adjustment. The filtered product may be classed as blue powder, but it contains only a trace of oxide. The filter bag gave no trouble and did not require cleaning.

Raw Materials and Their Preparation

The materials tested and their analyses are listed in Table 4. If properly prepared, all these materials give satisfactory results. Ores 1 and 3 contained so much dust that excessive pressure was required to force adequate flow of gas through a charge in the retort. For commercial application of this process, it will be necessary to devise a method of sintering or other treatment to eliminate most of the dust. For experimental purposes the material was just passed over a 120-mesh shaking screen and the undersize rejected. Most of the sulphur content of a properly roasted ore is present as sulphate. Sulphur combined as ZnS is affected only slightly by the reactions in the retort, but oxidized sulphur is changed to volatile compounds (H_2S, SO_2, etc.) which foul both the catalyst and the condenser.

Pretreatment is very simple. The roasted material is charged into a vertical iron retort heated to 800° C., and the exit gas from the condenser ($CO + H_2$) is passed through it until the fumes change from dark chocolate brown to white or pale yellow. The lower portion of the charge is then removed, more ore added at the top, and the treatment continued. Only part of the sulphur is volatilized, but that remaining is reduced to inert ZnS. The pretreatment expels most of the cadmium and partly reduces the iron oxide.

TABLE 4.—*Materials Tested*[a]

Constituent	Sintered Concentrates		Calcined Concentrates
	1 (Amer. Smelt. & Ref. Co.)	2 (Amer. Zinc & Lead Co.)	3 (Eagle-Picher Co.)
Zn	69.10	70.60	68.68
Pb	0.43	0.70	1.18
S	0.70	1.00	0.98
Cd	0.01	0.28	0.02
Fe	7.35		1.97
Cu	0.80		1.07
SiO_2	1.96		5.60
CaO + MgO	1.07	0.83	2.12

[a] In addition to the commercial ores listed, zinc-galvanizing dross was treated.

The galvanizing dross required different treatment in the same equipment. A mixture of air and steam was passed through the heated charge. The dross contains metal, which should be completely oxidized, and zinc chloride, which must be expelled or hydrolyzed into zinc oxide and HCl. Usually the pretreatment was carried on while the retort was operating, so that the exit gas could be used without storage. The quantity of exit gas more than suffices, and only a small portion of the gas is oxidized by the reactions in the pretreater.

Ore 1 has a high iron content (7.35 per cent Fe) and the reduction of this iron consumes a considerable portion of the gas required for reduction. The iron is partly reduced in the pretreater, but it is in a fine, spongy condition, so that atmospheric reoxidation is rapid if it is discharged hot.

Residues from this ore contain 30 per cent metallic iron, which in the lower part of the retort tends to sinter and form lumps that obstruct discharge of residues. To overcome this trouble and to increase the porosity of the charge, crushed coke was mixed with the ore in the ratio of 1 to 20. This coke enters into the retort reactions only to a minor extent, most of it being discharged with the residues, as well as considerable carbon from the gas.

When the flow of gas through the retort is stopped reactions 3, 4, 7 and 8 continue as in the usual method of reduction by carbon, but the rate of reduction is only a small fraction of the rate during normal operation with gas. This is positive evidence that at a given temperature the reduction with gas is much more rapid than reduction with carbon.

EXPERIMENTAL DATA

Tables 5 and 6 summarize data from two representative furnace runs. In comparing these results, especially the zinc content of the residues with those obtained in commercial plants, it should be noted that these residues are not diluted by large amounts of coal and therefore have a higher zinc content for a given extraction. The calculations in Table 7 show this effect of dilution.

TABLE 5.—*Zinc-furnace Data*

TEST, JULY 26–31, 1933

Initial Charge		Left in Retort		Residues Discharged	
Weight, Grams	Zinc, Per Cent	Weight, Grams	Zinc, Per Cent	Weight, Grams	Zinc, Per Cent
1340	50.4	1310	41.0	870	30.0
1100	47.4	1740	28.1	960	22.5
720	39.8	1210	21.6	920	10.4
1730	34.0	750	16.4	970	9.6
2560	30.4	360	10.7	1010	9.3
7450	38.2	5370	26.95	4730	16.05

	Weight, Grams	Zinc, Per Cent	Zinc, Grams	Zinc, Grams per Hour
Initial charge (residue)	7,450	38.2	2,846	
Operating charge, ore	23,290	67.8	15,800	145
Operating charge, coke	1,165			
Total charged	31,905		18,646	
Residues left in retort	5,370	26.95	1,447	
Net charge	26,535		17,199	158
Residues discharged	4,730	16.05	759	7
Extracted	21,805		16,440	151
Zinc recovered			15,400	141

Net operating time, 109 hr. Retort temperature, 1040° C. Gas used, 5300 liters (48.6 liters) per hour. Zinc per liter, 3.11 grams. Average composition of exit gas: CH_4, 0.5 per cent; CO_2, 0.3 per cent; H_2, 63.8 per cent; CO, 35.4 per cent.

The retort used in these experiments holds about 6 kg. of partly treated ore, more or less according to the grade of material, of which about 4 kg. is in the reaction zone. In Table 5 the average grade of the furnace charge is about 32.5 per cent zinc, [(38.2 + 26.9)/2]. Table 7 shows that this indicates 85 per cent extraction, and that of each 235 grams charged (the rate per hour) only 64 grams remains. The time required for the material to pass through the retort is therefore $^{6000}/_{64}$ = 94 hr., and through the reaction zone, $^{4000}/_{64}$ = 62½ hr. For these reasons, the zinc content of residues obtained during the first two or three days of operation is no criterion of the extraction because it depends mainly upon the composition of the initial charge. Since in this test (Table 5) the initial charge contained twice as much zinc as the final charge, zinc was extracted at a higher rate than it was charged as ore. In estimating the percentage of extraction we have the following alternatives:

TABLE 6.—*Zinc-furnace Data*

TEST, OCT. 12–19, 1933

Initial Charge		Left in Retort		Residues Discharged	
Weight, Grams	Zinc, Per Cent	Weight, Grams	Zinc, Per Cent	Weight, Grams	Zinc, Per Cent
780	38.0	2100	53.8	1410	6.1
650	34.1	1720	41.2	1575	27.2
680	25.4	1350	39.5	1070	38.6
540	21.0	1190	17.5	880	41.3
1180	10.9	640	20.1	1200	44.2
1350	6.2			1400	37.5
5180	21.0	7000	38.6	7355	31.1

	Weight, Grams	Zinc, Per Cent	Zinc, Grams	Zinc, Grams per Hour
Initial charge	5,180	21.0	1,088	
Operating charge, ore	30,150	67.8	20,417	156
Operating charge, coke	1,520			
Total charged	36,850		21,505	
Residues left in retort	7,000	38.6	2,702	
Net charge	29,850		18,803	144
Residues discharged	7,535	31.1	2,343	18
Extracted	22,315		16,460	126
Zinc recovered			15,950	122

Net operating time, 131 hr. Retort temperature, 1030° C. Gas used, 5250 liters (40.0 liters per hour). Zinc per liter, 3.12 grams. Average composition of exit gas: CH_4, 1.7 per cent; CO_2, 0.1 per cent; H_2, 60.4 per cent; CO, 37.8 per cent.

$$\text{Zn extracted/Zn charged} = {}^{151}\!/_{145} = 104 \text{ per cent}$$
$$\text{Zn extracted/net Zn charged} = {}^{151}\!/_{158} = 95.5 \text{ per cent}$$

Obviously the first is incorrect; the second is a good approximation, but it is influenced by residues that were not treated in this test. The net zinc charged is the sum of the zinc extracted and the zinc in the residues. Also, the zinc content of residues obtained *after* the first three days

Table 7.—*Calculation of Zinc Content of Residues*[a]

Charge	Extraction, Per Cent	Zinc, Grams	ZnO, Grams	Gangue, Grams	Fuel Residue, Grams	Weight, Grams	Zinc, Per Cent
100 grams ore...	80	13.6	17.0	14.0	0	31.0	43.9
0 gram coke...	85	10.2	12.7	14.0	0	26.7	38.2
	90	6.8	8.5	14.0	0	22.5	30.2
	95	3.4	4.2	14.0	0	18.2	18.7
100 grams ore...	80	13.6	17.0	14.0	5	36.0	38.8
10 grams coke..	85	10.2	12.7	14.0	5	31.7	32.2
	90	6.8	8.5	14.0	5	27.5	24.7
	95	3.8	4.2	14.0	5	23.2	16.4
100 grams ore...	80	13.6	17.0	14.0	25	56.0	24.3
50 grams coke..	85	10.2	12.7	14.0	25	51.7	19.8
	90	6.8	8.5	14.0	25	47.5	14.3
	95	3.8	4.2	14.0	25	43.2	8.8

[a] Assume ore, 68 per cent Zn, 14 per cent nonvolatile gangue; coke, 50 per cent left in residue.

is 4 grams per hour. Therefore, if the initial charge had been the same as the final charge, or if the same operating conditions were maintained for an infinite time, either method of calculating extraction would give the following correct result:

$$\text{Zn extracted/net Zn charged} = \frac{151}{151 + 4} = 97.5 \text{ per cent}$$

The situation in the run starting Oct. 12 (Table 6) is exactly reversed. The initial charge contains less zinc than the final charge; zinc is fed at a higher rate than it is distilled, and the first residues are of lower grade than later ones. The extraction, calculated as in the first section of the Table, is 80 per cent; zinc extracted, divided by net charge, is 87.5 per cent. If the net charge is based upon residues obtained after the third day, the extraction is about 85 per cent.

Residues containing less than 10 per cent zinc (better than 97 per cent extracted) have been obtained frequently over periods of several days; this is conclusive evidence that remarkably high extraction by this process is feasible.

In these tests a considerable portion of the zinc remains in the condenser, and accurate determination of the quantity of zinc condensed is not practicable. In Tables 5 and 6 the items for zinc recovered are based upon the zinc actually tapped plus a conservative estimate of the content of the condenser. Unless there is a gas leak in the apparatus the zinc condensed as metal must be about 99 per cent of the actual zinc extracted. A small portion is reoxidized, and still less is caught as dust in the filter. *There are no other sources of loss.*

The following data on smelting losses in present conventional retort practice were obtained from a large operator and show a net recovery of 86 per cent:

	Per Cent
Direct recovery of metal	66.0
From resmelting blue powder	20.0
Loss in resmelting blue powder	2.5
Loss in residues containing 14 per cent Zn	6.0
Absorbed in retorts and condensers	2.0
Failure to condense	2.0
Unaccounted-for loss	1.5

Capacity

Rates of reaction increase rapidly with temperature. They are also affected by the composition of the charge and by the rate of gas input. Feeding ore at a high rate will increase the zinc content of the charge and the rate of reaction, but will decrease the percentage of extraction. A high rate of gas input will increase reaction rate but decrease the zinc extracted per unit volume of gas. Therefore, when efficiently operated, the capacity of a retort is determined by its temperature, and the latter is limited to 1100° C. by the thermal limit of the metal used in constructing the retort.

In the experimental unit, 1050° C. was considered the upper limit for safe operation to allow for fluctuations in heat input and local overheating. At that maximum temperature the zone above 1000° C. extended over only half the heated length. The reaction zone (above 900° C.) of 170 cu. in. had an average temperature of 1010° C. The production of metal (with 97 per cent extraction) was 3620 grams per 24 hr. or 21.2 grams per cu. in. per day. On this basis, a retort 8 in. in diameter and 54 in. long would produce 122 lb. of metal per day. With lower extraction a much higher reaction rate has been obtained.

In a large unit the zone of maximum temperature would extend over a much larger portion of the reaction zone, and with adequate temperature control the average temperature could be increased to 1050° C., which would about double the reaction rate and capacity. The temperature drop from the heating chamber to the center of an 8-in. retort is about 10° C.

Gas Pressure

The pressure required to force an adequate flow of gas through the ore charge and bed of catalyst varied considerably with different ores and with different operating procedures. In general, conditions favoring high reaction rate, such as a densely packed and finely divided charge or an increase in temperature, also require an increase in gas pressure. Operating conditions giving the data in Table 5 required an average gas pressure of less than ½ lb.; in most tests, the pressure averaged 1 lb. and in some tests reached 5 lb. The pressure drop through the catalyst usually is about one-half the total.

Calculations based upon studies by Furnas[7] of relations between the temperature, the dimensions of the retort, the sizing of the charge, and the rate and pressure drop of the flow of gas give surprising results. A change in only the diameter of the retort will have no effect on the rate of flow per unit of area; but if the length is doubled, the rate of flow must be doubled (to maintain an excess CH_4 for the catalytic reactions), and the pressure drop will be four times as large.

From these estimates it appears that 16 ft. is about the limit of retort length for practical gas pressure, unless a radical change is made in the preparation of the ore charge. In this connection, the pressure decreases rapidly as the size of the ore grains increases, and a mixture of large lumps in a bed of fine particles offers a much greater resistance to the flow of gas than if the large lumps were absent. The minimum resistance is found from the maximum average size of particles and a minimum difference between the various sizes.

In a large retort with automatic feed and discharge it should be possible to maintain a more uniformly distributed charge than by intermittent manual operations. Moreover, in a large unit the pressure drop in the ends of the retort will be a smaller fraction of the total than in the experimental unit.

There are not yet enough data upon which to base precise calculations of the most effective dimensions of a catalyst chamber, but if the form and size chosen are approximately correct, the catalytic rate can be varied by changing the size of the grains of catalyst.

DESIGN FOR LARGE FURNACE

Figs. 10 and 11 are plans for a pilot plant that incorporate all the changes and refinements suggested by the work to date. Except in minor details, the design and materials of construction are exactly like the same features of the experimental furnace.

Sections of sheet-alloy parts are shown in the plans by extra heavy solid lines. All other sections are indicated in a conventional manner.

Heat Distribution.—Considerable attention was given to means of obtaining economical use and proper distribution of the heat. The gas burners are designed to use preheated air from a recuperator. A regenerative system would be less efficient and give less uniform results. The multiple combustion chambers enter the annular space around the retort tangentially through fan-shaped ports so staggered as to distribute the heat uniformly and produce a maximum velocity of rotating motion (Fig. 11*a*).

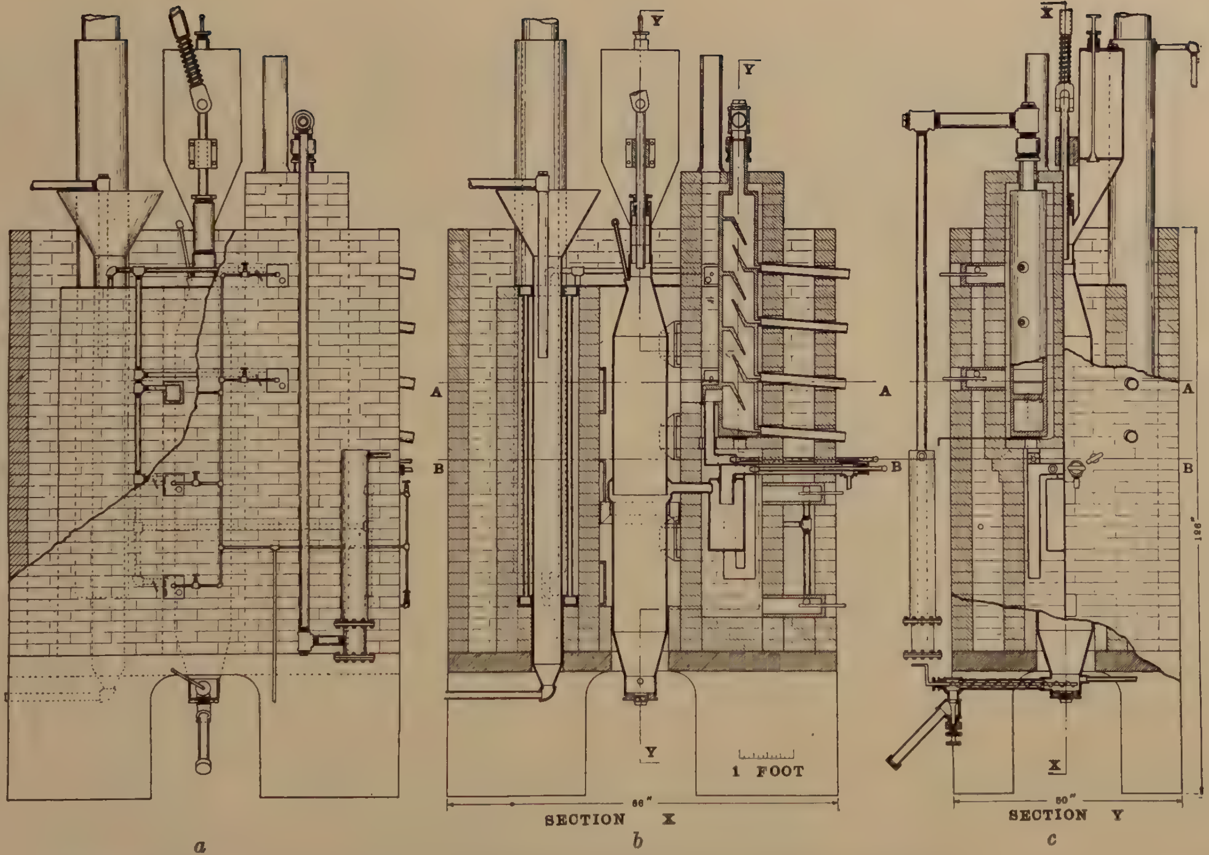


FIG. 10.—PILOT PLANT FOR REDUCTION OF ZINC ORE BY NATURAL GAS.
a, side view (outer wall partly removed); *b*, side view, axial section at *X* (see *c* and Fig. 11*a*); *c*, end view (cut at various sections).

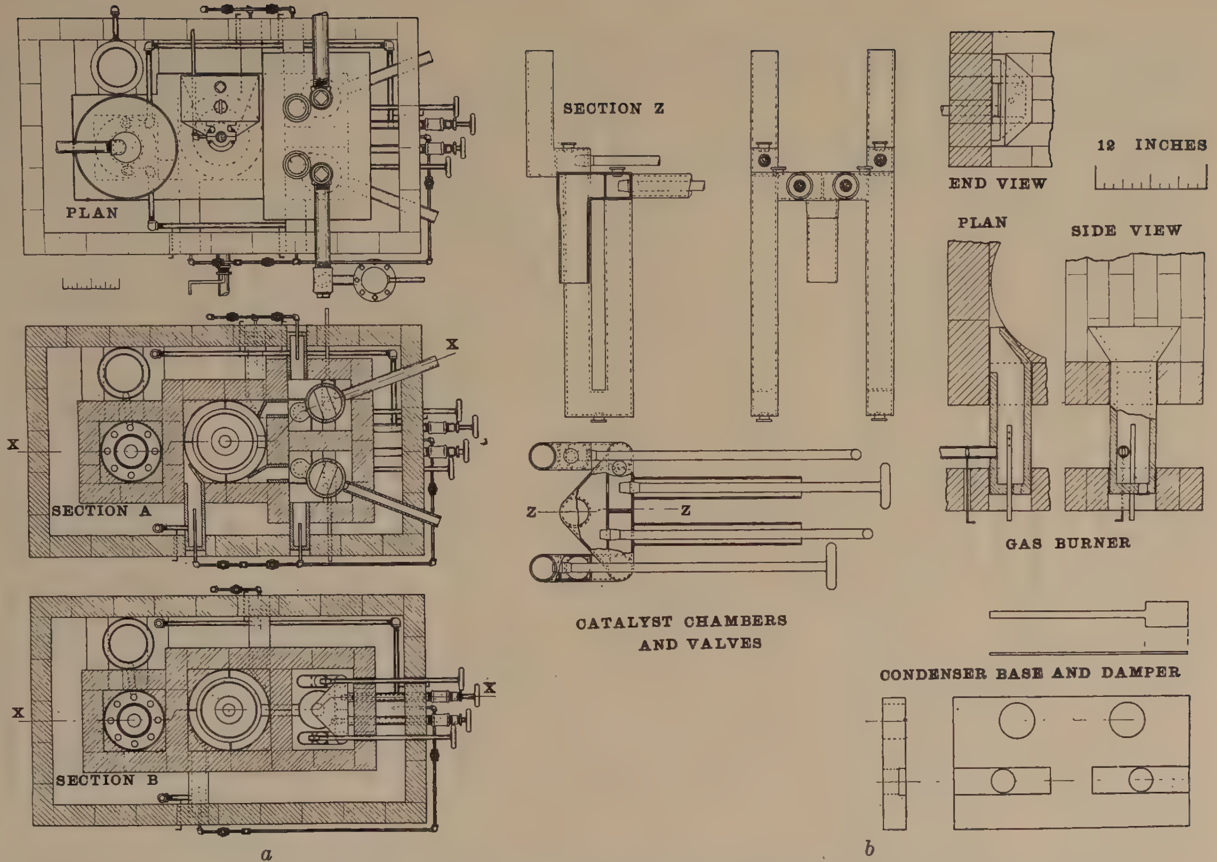


FIG. 11.—PILOT PLANT FOR REDUCTION OF ZINC ORE BY NATURAL GAS.
a, plan and horizontal sections *A* and *B* (see Fig. 10*b* and *c*); *b*, details of catalyst chamber, gas burner and condenser base.

The combustion products spiral upward around the retort and pass through a port in the top of the wall which separates the retort from the pretreatment kiln (to the left). The kiln is a 6-in. alloy tube surrounded by eight ¾-in. alloy recuperator tubes, joined top and bottom to annular distributing flues. The heating gases pass downward through this chamber and then back through a short flue to the stack (in the left rear corner of the plan). The stack has a double wall, which provides an annular recuperation space through which air for the gas burners is forced downward, then up through the recuperator tubes, and finally distributed to the burners through pipes placed in the insulated space between the inner and outer furnace walls. In this manner, most of the heat content of the gas fuel can be utilized.

Two other burners heat the catalyst chamber. A portion of the heating gases from this chamber passes through ports (with regulating dampers) in the condenser base (Fig. 11*b*) so that the temperature of the lower part of the condensers can be controlled. The larger portion of the heating gases travels upward around the flue leading to the condenser and is then deflected by an alloy shield into ports leading to the retort chamber. The temperature of the upper part of the condensers is controlled by additional burners, through which either heat or cold air may be supplied.

Automatic temperature control for the retort and catalyst would be desirable but not essential if a constant-pressure gas supply is provided. A very liberal supply of pyrometer thermocouples should be installed in an experimental unit.

Charging and Discharging Mechanisms.—The ore-charging device is not a tested design. It consists of a reciprocating plunger which enters the top of the retort through a stuffing box. Motion is imparted by a crank or cam (not shown) through a connecting rod consisting of a shaft and sleeve with a stiff spring so placed that it will relieve excessive pressure on the plunger by a compression allowing the sleeve to slide on the shaft. Ore from the gastight hopper will drop under the plunger and be forced down by its motion. The latter may be adjusted to feed slightly more than is required, and the spring will compensate for the excess. The ore hopper contains a partition with a port sealed by a bell valve, so that ore may be supplied to the hopper without releasing the gas pressure in the retort.

The discharging device consists of a simple screw conveyor having a gastight stuffing box for the conveyor shaft. A small gastight hopper is connected to the conveyor pipe by a 45° tee provided with a special valve so that the hopper can be emptied without releasing the gas pressure in the retort. A hand crank is shown as a means for operating the conveyor screw, but a very slow mechanical drive is preferable. This device has been tested and works satisfactorily.

Retort.—The retort consists of an upper cone welded to a 12-in. tube 36 in. long. A lower cone is welded to a 12-in. tube 30 in. long. The two parts are joined by a ring 14 in. in diameter, which is flanged inward and welded in the position shown. The upper tube extends into the middle ring, forming an annular offtake for the retort gases. Feed and discharge mechanisms are connected by pipe couplings welded to each end of the retort. Gas-inlet connections are welded to these couplings.

Dust Collector.—A flue 3 in. in diameter and 8 in. long connects the gas offtake of the retort with a dust trap 8 in. in diameter and 16 in. long, constructed like a cyclone collector. The gas inlet is covered by a baffle, which deflects the gas tangentially to give a centrifugal effect. The gas outlet is a short 3-in. pipe, which is part of the catalyst-chamber assembly (Fig. 11*b*). It projects into a central opening in the top of the dust chamber, which has a tapered collar that makes a gastight joint with a tapered shoulder on the outlet pipe.

Experience has shown that only a very small amount of dust reaches the dust collector. Although this dust will affect the gas pressure appreciably if it is deposited in the bed of catalyst, accumulation of enough to fill the dust chamber requires an exceedingly long time. If necessary, a clean-out port may be cut in the bottom of the collector and be machined to fit a tapered plug with a handle extending down through the base of the furnace. By this means the accumulation of dust could be blown out of the chamber whenever necessary.

Catalyst Chambers.—There are two U-shaped catalyst chambers constructed of 3-in. pipe. Each U is 24 in. high. One leg of each U is welded to a header, which in turn is welded to the offtake flue from the dust chamber. The header is divided into two valve chambers, by partitions. By means of the valves gas from the retort may be admitted to, or cut off from, either of the two catalyst chambers. The valve stems project through pipes welded to the header. These pipes admit gas for regenerating the catalyst or cleaning a condenser. During these operations the valve is pushed inward, and for normal operation the valve is pulled outward.

The second leg of each U is offset at the top to form another valve chamber for each catalyst. Vertical flues lead from these valve chambers to the condensers. The purpose of the valves is to close the passage to the condenser and provide a by-pass for gases used to regenerate the catalyst. During normal use, or when a condenser is cleaned, the valve is pulled outward. To prevent fouling of the condenser during regeneration of the catalyst the valve is pushed inward to close the condenser passage and open the by-pass, so that the gases escape through the opening around the valve stem into the heating chamber.

Openings for removing and charging catalyst are provided at the top and bottom of each U. These openings are closed by tapered plugs so fitted as to make a gastight seal when coated with waterglass and firmly seated.

Valves.—The valves are of a peculiar design, developed for this particular service. They are not especially difficult to make. They are two-way valves, having two valve seats, one corresponding to that in a globe valve and the other in the by-pass opening through which the stem projects. The valve disk is simply an enlargement of the stem tapered at 5° in both directions to fit corresponding tapers in the valve seats. They are made of alloy sheet and welded.

Condensers.—The condensers are constructed of porcelain in a cylindrical shape 9 in. in external diameter. Partitions deflect the flow of gas and provide four traps for collecting metal. A porcelain elbow projecting from the lowest section of the condenser joins the gas-inlet port to the metal flue leading from the catalyst chamber.

A compression gland is attached to the upper 4-in. porcelain extension of the condenser, making a gastight joint between the condenser outlet and the flue leading to the dust collector. This flue, of 3-in. and 2-in. iron pipe, cools the hot gas from the condenser before it reaches the wool filter bag.

The filters (one for each condenser) are single-unit bag filters of conventional design, with a 5 by 36-in. bag enclosed in a 6-in. cylindrical metal housing. A 1-in. gas-outlet pipe leads from the filter to a gas-storage tank (not shown).

Multiple Units.—The furnace is thus provided with two sets of catalyst chambers, condensers, filters, and connecting flues and valves. This may appear rather elaborate for a pilot unit, but experience has shown that it is essential to uninterrupted service. In a commercial plant with multiple retorts, the gas from each retort would enter a common flue leading to a battery of catalyst-chamber and condensing systems having only one or two units in excess of normal operating capacity. The cost of the extra units would be nominal compared with the expense of more or less frequent interruptions. While the duplex feature in an experimental unit may not be justified from a cost standpoint, it is necessary to test the details of construction and operation.

Pretreatment Kiln.—The pretreatment kiln is heated by waste gas from the retort chamber, which should be enough to maintain a temperature of 850° C. Since adequate pretreatment can be accomplished anywhere between 750° and 950° C., means of regulating the temperature have not been indicated but may be supplied if required.

Mechanism for discharging the ore from this kiln is not shown in the plans, but it can be the same as that used in the retort. An inlet for condenser-exit gas enters the bottom of the kiln. The open upper hopper is kept full of ore. To prevent reoxidation and deposition of volatilized impurities in the cold upper part of the charge the gaseous products are drawn off through a 2-in. pipe extending into the hot zone. These gases may be led to a bag filter connected to the suction end of a pressure blower (not shown).

This final exit gas, consisting largely of CO and H_2, will still contain a large fraction of the B.t.u. value of the gas fed to the retort, and more than the endothermic requirements of the process. It may be used as a source of heat, or a more valuable use as a metallurgical reagent in some auxiliary process may be developed.

The cost estimate in Table 8, for the construction of one large unit, was made with the assistance of an independent engineer.

TABLE 8.—*Estimated Cost of One Large Unit*

	Material	Labor	Total
Retort	$ 90	$ 40	$ 130
Charging mechanism	270	100	370
Catalyst chamber and valves	60	80	140
Pretreater and recuperator	70	30	100
Gas-circulating equipment	650	100	750
Gas burners, etc	140	110	250
Refractories	575	275	850
Miscellaneous	400	400	800
Total	2255	1135	3390
Unforeseen			710
			$4000

ECONOMIC POSSIBILITIES

The technical feasibility of the process has been demonstrated thoroughly on a laboratory scale, but the economic possibilities can be determined only by tests in a larger unit. The following estimates are based on laboratory data (and in many details are only approximations):

Capacity.—The capacity per unit of retort volume is chiefly a function of temperature. Since the average temperature of a large retort may come closer to the safe maximum temperature than is possible in the laboratory size, probably it will have a higher rate of reaction. Based upon the capacity of the 3-in. retort, the 12-in. retort will produce about 300 lb. of zinc per day. This might be doubled.

Recovery.—Undoubtedly an extraction of 95 per cent is feasible, and nearly all the zinc extracted will be recovered as metal.

Utilization of Gas.—Five cubic feet of gas will produce about one pound of metal.

Fuel Consumption.—The amount of gas required to heat the laboratory furnace was excessive and cannot be used as a basis for estimating fuel consumption in a large unit. The fuel required per pound of zinc certainly will be much less than (perhaps half) that required to heat the present type of commercial furnaces because: (1) The operating temperature is at least 200° lower; (2) radiation loss is practically eliminated; (3) the thermal conductivity of the retort is incomparably greater as the denser charge and hydrogen content of the retort improves transmission of heat through the charge; (4) continuous operation is thermally more efficient; (5) much larger capacity per unit volume of retort; (6) the heat value of the condenser exit gas.

These factors are offset to some extent by the heat required for pretreatment, catalysis and to raise the reduction gas to reaction temperature.

Life of Retort.—The cost of retort replacement is one item that may and probably will exceed the equivalent item in present practice. It is a most uncertain factor. During intermittent laboratory tests over a period of two years two retorts failed. The last retort constructed has given more service than both the other two and still is usable. The failure of one retort was caused by treating dross containing chlorides. The first failure occurred in a rectangular retort and started in the welded joints. Cylindrical shapes are more durable. Accidental overheating may partly account for the failure; but the retort metal was brittle, even where overheating was impossible.

Deterioration of the metal, as shown by crystal growth and brittleness, may result from heating. Chemical reaction with carbon, sulphur and zinc also is possible. There appears to be little or no reaction with zinc vapor, but if liquid zinc comes in contact with hot alloy the latter is ruined. During normal operation such contact does not occur, but when a retort is cooled after a run is completed zinc metal is condensed on the wall, and when heated for a subsequent test it alloys with the retort metal. This contact with liquid zinc, and alternate heating and cooling, probably is a more severe strain on the retort than continuous service would be. The retort will probably last longer at 1000° C. than at 1050°, but the capacity will be less. Data covering years of operation will be required to determine the best alloy and the temperature at which the operating cost (including replacement of retorts) per pound of zinc is lowest. At the present cost of alloy metal (50¢ per pound) a retort and catalyst chamber will cost about $270, to which $30 may be added for time lost. Assuming a life of one year and a production per retort of 300 lb. of zinc per day, the replacement cost will be 0.28¢ per pound of zinc. Increase in capacity or in size of retort will decrease replacement cost. Also, 50¢ seems a high price for chromium-iron alloy, and it may become much cheaper.

Life of Condensers.—Condensers will require occasional cleaning (by distillation) and unless accidentally broken should last indefinitely. The replacement cost may be neglected.

Life of Refractories.—At the relatively low furnace temperature, a well built furnace should last indefinitely.

Life of Catalyst.—No limit has been found for the life of the catalyst. Regenerated material seems to be as effective as freshly made catalyst. The cost of replacement would be mostly the cost of closing down the furnace and obtaining access to the catalyst chamber.

Labor.—Common labor can almost be eliminated, and working conditions will be infinitely better than in present plants. After details of operation have become standardized and automatic control of temperature, feed, discharge, etc., has been adjusted, technical supervision should not be difficult. One trained and one untrained man could operate a large number of units.

Quality of Products.—The zinc produced is nearly as pure as electrolytic metal. Lead, mixed with a little zinc, is obtained as a separate product. Cadmium can be recovered from pretreatment fume.

Cost of Installation.—The initial cost of a furnace for gaseous reduction may be more than an ordinary furnace of the same capacity, but the former will have a much longer life because of the lower furnace temperature. Expensive machinery is not required for making retorts and condensers.

Pretreatment of Ores.—It appears certain that a suitable preparation for most ores will include a sintering roast, followed by screen sizing, crushing the oversize, and return of undersize to the sintering step. In this manner a granular, porous, closely sized material will be obtained.

If the gangue is high in iron or becomes "sticky" at 1050° C. for other reasons, it may be necessary to dilute the charge with some inert, infusible material, such as coke or lime. In recent experiments on the production of sponge iron it was found that a wash with milk of lime is an inexpensive and practical means of preventing sintering. This may be applicable to zinc ores that tend to hang up in the retort.

Pretreatment with exit gas to eliminate sulphates will be necessary. The value of the cadmium that can be recovered by this operation may be more than the small cost of treatment.

Mechanical Feed and Discharge of Ore.—Development of satisfactory mechanism for the charging and discharging may take time. The retort charge must not be allowed to have empty spaces or be packed too tightly. Proper preparation of the ore is essential for satisfactory operation of feed and discharge.

Electrothermic Reduction.—A combination of electrothermic and gaseous reduction has possibilities. By the use of internal, electrothermic heat, much larger retorts can be used and the average temperature of the charge can be increased without overheating the retort. This would increase the capacity and greatly reduce the cost of replacement per pound of zinc.

Economic Possibilities.—Additional quantitative data on the following points would permit an unequivocal decision as to the final economic possibilities of the process:

1. Effects of temperature variations, relative volumes and rates of gas flow in the upper and lower parts of the reaction zone on capacity, extraction and catalytic reactions.
2. Effect of rate of ore travel on capacity and extraction.
3. Effect of ore impurities, retort temperatures and recirculation of exit gas on catalytic reactions.
4. Effect of size and shape of catalyst chamber on catalytic efficiency.
5. Effect of temperature on the life of retort.

Adequate data on these points require precise automatic control of temperatures, rates of gas flow, feed and discharge of ore, and the operation of a unit under regular conditions for sufficient time to determine the life of the unit. While it would not be impossible to provide the necessary refinements and obtain these data with laboratory equipment, neither personnel nor the funds were available during these experiments, and it further seems that the data can be more effectively determined during the pilot-plant tests, which are still thought to be a necessary preliminary to a commercial development of the process.

SUMMARY

A new process for reduction of zinc ores by natural gas has been tested and the results prove that it has many points of superiority over existing methods. All the reactions involved were intensively studied thermodynamically and as to rates. An apparatus of maximum laboratory size was built and an operating technique was developed, which permitted a satisfactory continuous operation of the process. All the details of construction and operation are well adapted to a commercial use.

Many tests were made on several typical zinc ores and on galvanizing dross, in several of which the furnace was operated continuously for more than 100 hr. The capacity of a 3-in. (diameter) retort was over 200 grams of ore per hour. Five cubic feet of gas produces one pound of metal. Over 95 per cent of the zinc is readily extracted.

All the difficulties encountered (some of which were baffling and discouraging) were finally overcome. In solving these difficulties two fundamental innovations were developed which seem to be absolutely essential to any practical process in which zinc ores are reduced by natural gas. The most important innovation consists in preventing reoxidation by catalyzed reactions and the development of a satisfactory technique for maintaining those reactions at maximum efficiency. The second innovation is the combination of a concurrent travel of ore and gas in the first part of the reaction zone followed by a countercurrent travel of ore and recirculated exit gas in the second stage of the reaction. This makes it possible to obtain simultaneously high utilization of the gas and very high extraction of the zinc.

Other essential improvements include the development of a condenser adapted to the exacting needs of the process and a method of pretreating the ore to eliminate certain impurities.

REFERENCES

1. H. A. Doerner, G. L. Oldright, T. B. Brighton and C. L. Dice: Studies in Zinc Metallurgy. U. S. Bur. Mines *R.I.* 3256, Progress Repts., Met. Div., 8. U. S. Patents 1961424 and 1961425.
2. C. G. Maier: Zinc Smelting from a Chemical and Thermodynamic Viewpoint. U. S. Bur. Mines *Bull.* 324 (1930).
3. H. A. Doerner: Reduction of Zinc Oxide by Methane or Natural Gas. U. S. Bur. Mines *R.I.* 3091 (1931).
4. D. M. Liddell: Handbook of Nonferrous Metallurgy, **2,** 1209. New York. McGraw-Hill Book Co.
5. J. Chipman: Free Energy of Water, Carbon Monoxide, Carbon Dioxide, and Methane. *Ind. & Eng. Chem.* (1932) **24,** 1013.
6. H. A. Doerner and C. G. Maier: Recent Progress in Reduction of Zinc by Natural Gas. A.I.M.E. *Contrib.* 9 (1933).
7. C. C. Furnas: Flow of Gases through Beds of Broken Solids. U. S. Bur. Mines *Bull.* 307 (1929).

Direct-process Zinc Oxide

By E. H. Bunce* and H. M. Haslam,† Members A.I.M.E.

The "direct process" for the manufacture of pigment zinc oxide produces the oxide directly from ore. This is accomplished by reducing the zinc by means of carbonaceous fuels and immediately burning the evolved zinc vapor to zinc oxide. For many years this was done by smelting a loose charge of ore and fuel on perforated grates. Since this process was developed in America and was extensively used here, it has become known as the "American process."

Alternative methods of producing pigment zinc oxide are the "indirect process" and the "wet process." In the indirect process the raw material is metallic zinc, which is volatilized and burned to the oxide. For a long time this has been done in externally fired horizontal refractory retorts. This process has become known as the "French process," from the country of its origin.

The wet process precipitates the carbonate or hydrate from zinc-bearing liquors and then calcines the precipitate. This method has been but sparingly used for producing commercial quantities of zinc oxide.

It appears to be advisable to restrict the use of the terms "American process" and "French process" to the methods of the earlier periods and to consider the terms "direct process" and "indirect process" as generic terms to designate, first, all methods of producing pigment zinc oxide directly from ores, and, second, to include all those methods of producing zinc oxide from metallic zinc and metallic zinc-bearing substances.

American Process

In 1796 John Atkinson was granted British Patent No. 2094/1796 entitled, "Manufacture of White Paint." This patent describes a method of producing zinc oxide in which roasted zinc blende or calcined calamine is mixed with charcoal, and the mixture heated in a muffle to liberate zinc vapor, which is then burned to obtain zinc oxide fume.

About 1850 The New Jersey Zinc Co., at its plant in Newark, N. J., attempted to make zinc oxide by smelting, in a reverberatory furnace, a mixture of coal and ore from its Franklin mine. A considerable amount

---

Manuscript received at the office of the Institute Oct. 29, 1936.

* General Manager, Technical Department, The New Jersey Zinc Co., Palmerton, Pa.

† Chief, Metallurgical Section—Pigment—Research Division, The New Jersey Zinc Co.

of pigment was made in this way, but the procedure was not commercial. Later a method similar to that of John Atkinson's was tried. The product was better than that from the reverberatory furnace but the recovery of zinc was poor. The experiments at Newark eventually developed a process that was successful, which was called the Wetherill furnace method, after Samuel Wetherill, who developed the practical furnace and the process. At the same time S. T. Jones conceived the idea of collecting the zinc oxide. His plan was to cool the mixture of zinc oxide and gas and then filter through a muslin fabric. In this way "bagrooms" became associated with the collection of smelter fumes.

A flowsheet of the American process is shown in Fig. 1.

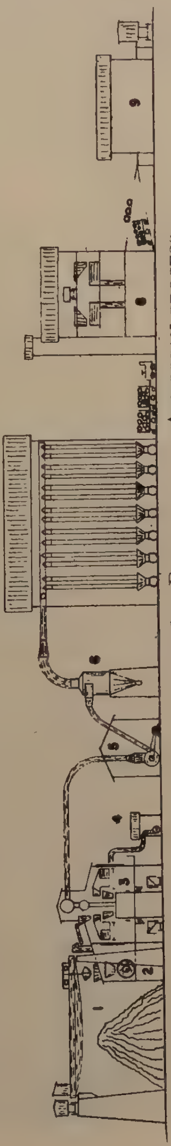


FIG. 1.—FLOWSHEET OF AMERICAN PROCESS.

1. Raw-material storage.
2. Mix house.
3. Oxide furnace.
4. Blow house.
5. Fan house.
6. Cyclone.
7. Baghouse.
8. Packing house.
9. Oxide storage.

THE WETHERILL FURNACE

Two types of Wetherill furnaces have evolved from the development and distribution of the industry; now known as the "eastern" type and the "western" type. These types differ only in design; their underlying principles are the same.

Eastern Wetherill Furnace

The eastern type of furnace (Fig. 2) unit consists of four or more small firebrick furnaces built together with a common back wall and common side walls into what is known as a "block." All furnaces of a block are operated simultaneously, though they are charged at different times and worked independently, according to a cycle of operations found economical for the prevailing conditions. The vapors from each furnace are removed through an opening in the arch and conducted to a separate section of a system of combustion chambers, where the zinc vapor is completely oxidized. From here they enter a common pipe line leading to a bagroom. By this means the product from individual furnaces is blended, and the material collected in the bagroom is the product of a "block" and not of a single furnace.

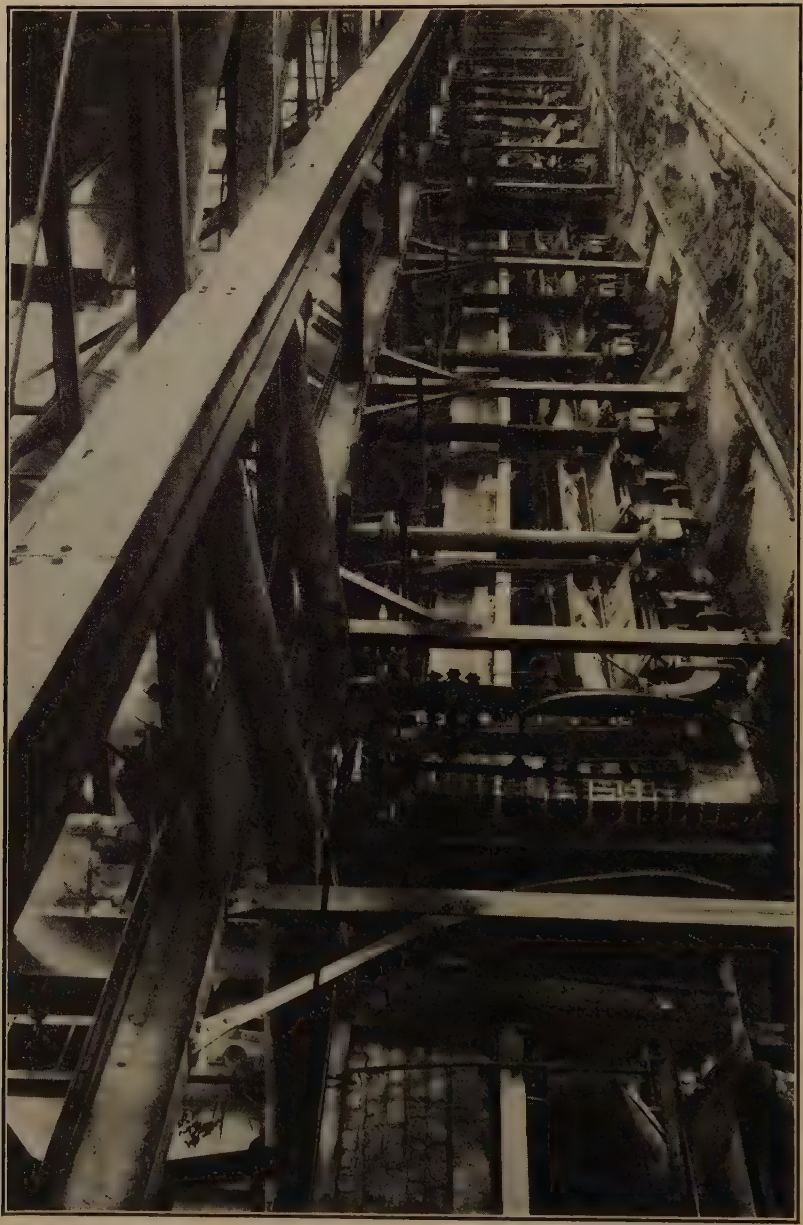


FIG. 2.—EASTERN TYPE OF FURNACE, GENERAL VIEW.

The operation of an eastern-type furnace is as follows: A predetermined amount of zinc ore and suitable fuel is thoroughly mixed in a mechanical charge mixer, with enough water to produce a satisfactory setting of the charge when it reaches the furnace. A charge that is too wet has a tendency to form top crusts, while one that is too dry loses too much of the fine materials by dusting.

The operating cycle of each furnace may be considered as starting with the removal of the clinker from the spent fire. This removal is carried out as rapidly as possible, so that the furnace will not lose too much heat. A thin layer of firing fuel is then spread over the cleaned, perforated grate, through which cold air is blown. This layer of fuel is soon ignited from the residual furnace heat. As soon as this fuel charge is well ignited, a charge of ore and fuel is placed on top of it and leveled off. It is necessary that the furnaceman watch this new charge carefully in order to ensure even ignition and working of the zinc. It is desirable that the elimination of the zinc be carefully controlled, so that the charge will be worked off in accordance with the predetermined time schedule. The time of efficient operation varies according to such factors as character of ore being treated, design of furnace and quantity of charge (or burden).

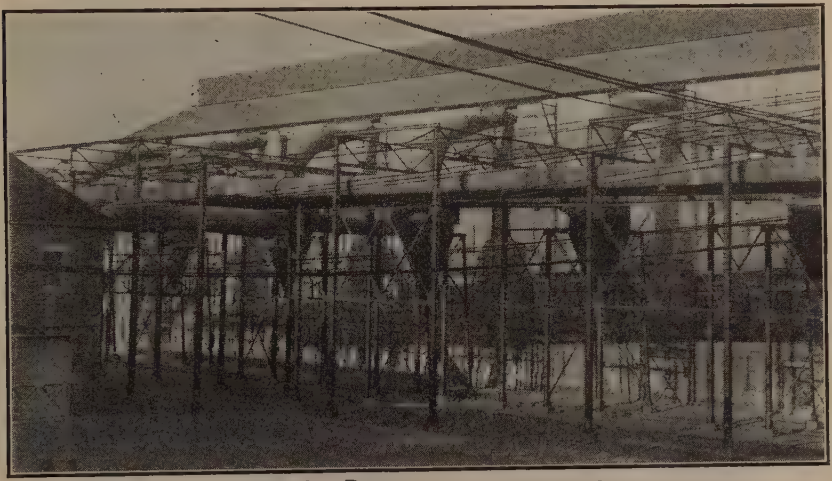


Fig. 3.—Pipe line and baghouse.

As the fumes of zinc oxide arise from the charge, mixed with the products of combustion from the fuel, they enter a system of sheet-iron pipes which run from the furnace top to a collecting room, or bagroom (Fig. 3). Somewhere in this pipe line, usually near the bagroom, is placed a large fan, which is the moving agency of the gas system. From the fan to the furnace the pipe-line system is under suction, and from the fan to the bags it is under pressure.

The bagrooms are large one-room structures filled with vertical fabric tubes (Fig. 4). The furnace gases bearing the zinc oxide are blown into these bags. The gaseous products pass through the pores of the fabric and escape, while the oxide adheres to the bag surface and remains.

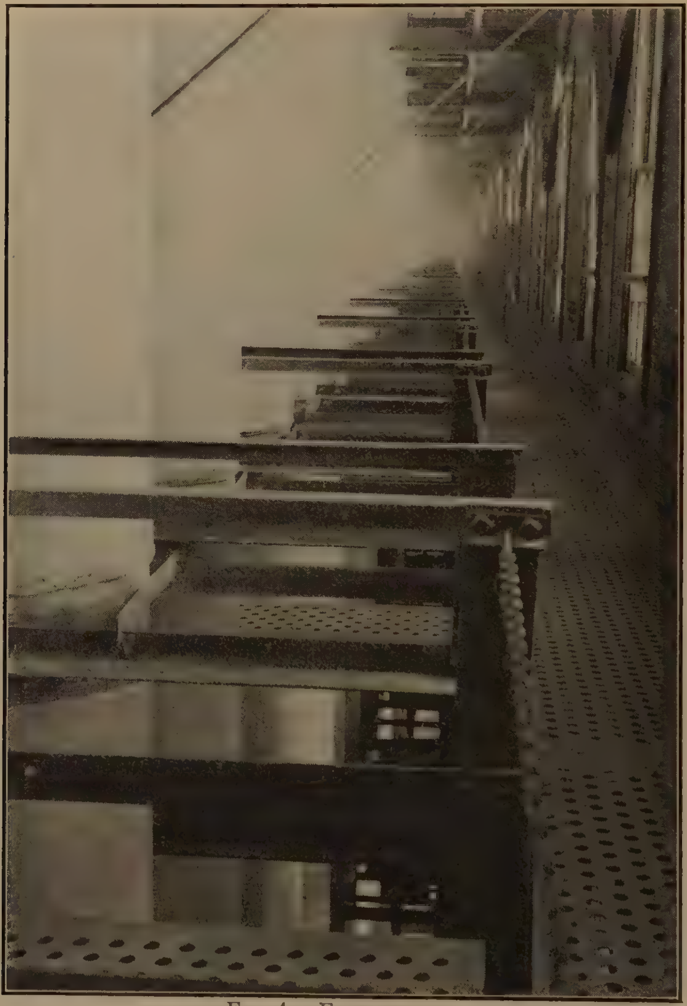


FIG. 4.—FILTER BAGS.

When the bags are violently agitated, the entrapped zinc oxide falls away and drops into collecting bags (Fig. 5) at the bottom of the bagroom. The collecting bags are periodically removed and replaced by empty bags. The loaded bag is then transferred to the packing room.

When the finished product from the collecting room (baghouse) is received by the packing house, it is screened (Fig. 6) and packed into paper bags or wooden barrels by means of an auger-type packing machine (Fig. 7). In this form it is shipped to the consumer.

Western Wetherill Furnace

The western type of furnace (Fig. 8) is designed so that the fumes from each of the twelve or more furnaces that comprise a block pass into a common overhead flue, which conducts them to the end of the block and into a common combustion chamber. This is the essential difference between the eastern and the western types. In both types the fumes are blended while passing through the connecting flues from furnace to collecting room.

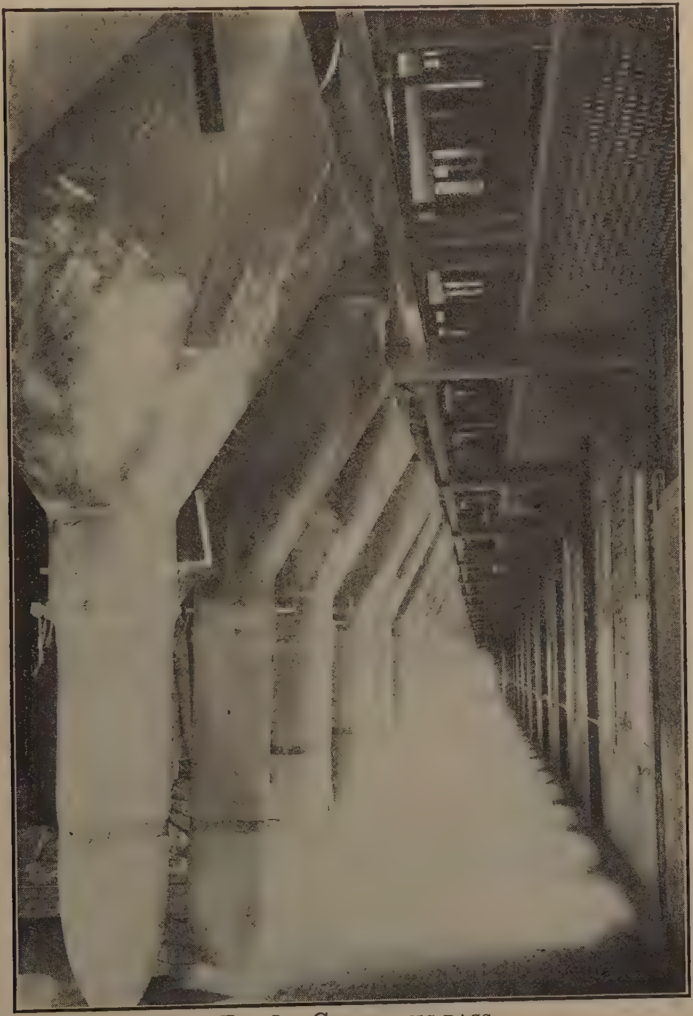


FIG. 5.—COLLECTING BAGS.

The present form of both furnace types of the American process is the result of a long series of improvements in the details of construction and operation (Fig. 9). These changes have resulted in higher quality of product and higher efficiency of operation. The introduction of mechanically operated charging and discharging machinery made it possible to treat heavier burdens and to increase the grate areas, thus increasing the size and yield of individual furnaces.

Raw Materials and Product

The raw materials that can be worked economically vary in zinc content from about 15 to 75 per cent. Impurities such as calcium, iron and silica affect the character of the clinker and influence the metallurgical results. Volatile constituents of the charge, even in small amounts, greatly affect the finished product. Fine sizes of anthracite coal are largely used in eastern-type furnaces but any small-sized smokeless fuel can be used with satisfactory results.

FIG. 6.—SCREENING ZINC OXIDE.

Zinc oxide is a white, nontoxic, slightly basic pigment of extremely fine particle size. Because of its unique characteristics, it is used in the manufacture of a variety of commodities, such as paint, rubber, linoleum, oilcloth, printing ink, ceramics, paper, textiles and cosmetics. In some of these applications its usefulness is due to its pigment properties; in others, its chemical activities predominate. The successful use of zinc oxide for such a varied range of products requires during its manufacture the most careful control of such properties as particle size, particle shape, color, brightness and smoothness. This means that there are and must be many grades of zinc oxide, each one designed and produced for the special use to which it is to be put.

TRAVELING-GRATE FURNACE

Since the various users of zinc oxide pigment demand various combinations of physical and chemical properties, the selection of the furnace type for the product of this combination is as important as that of the selection of the raw materials. A very important factor in the control of certain physical properties of the pigment is the rate of combustion of the charge. A free-burning open charge rapidly worked produces material different from that produced by a charge that is dense and slow working.

FIG. 7.—PACKING ZINC OXIDE.

A newer type of furnace, known as the traveling-grate type, has been designed, bearing in mind the desirability of controlling as many of the variable factors as possible. The necessity for developing a continuously operating furnace to produce zinc oxide by the direct process had long been felt by the industry, on account of the difficulties encountered in operating the Wetherill furnace, but no satisfactory solution of the many problems presented thereby was obtained until 1919, when the first completely mechanized zinc oxide furnace was constructed and successfully put in operation by The New Jersey Zinc Co. at its Palmerton plant.

Fig. 8.—Western-type furnace.

The mechanization of the direct process involves the continuous feed of raw materials into the reduction zone; the continuous production therein of zinc vapor that can subsequently be burned to zinc oxide; and the continuous removal of the zinc-free residue.

Early attempts failed chiefly because of inability to inhibit the accumulation of slag in the reduction chamber, which accumulation prevented smooth operation over any long period of time. This difficulty was overcome in the traveling-grate furnace by the adoption of a briquetted charge.

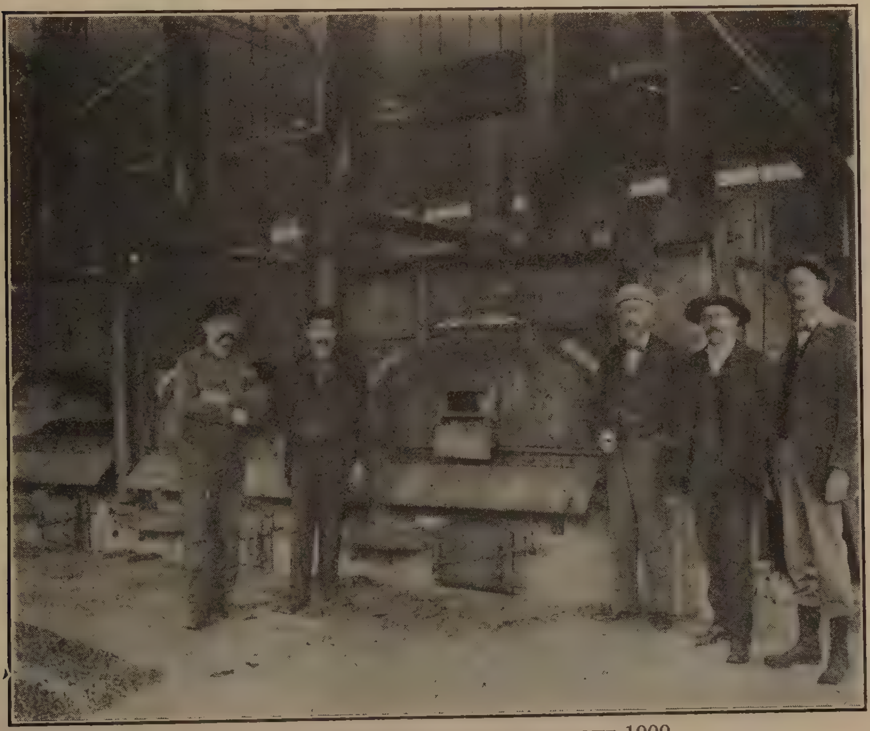


FIG. 9.—EASTERN-TYPE FURNACE ABOUT 1900.

The traveling-grate or mechanical process for the production of zinc oxide differs from the American process in two features: first, the preparation of the charge and, second, the furnacing of the charge.

Charge Preparation by Briquetting

Two types of briquettes are used in compounding the charge: ore briquettes (containing ore plus reducing fuel) and fuel briquettes. The reason for this will be made clear in the description of the furnacing of the charge.

The ores and the coal for the ore-briquetting plant are stocked in large bins close to the mix house. The ore used should be fairly fine. Zinciferous intermediate products may be used, of course, as sources

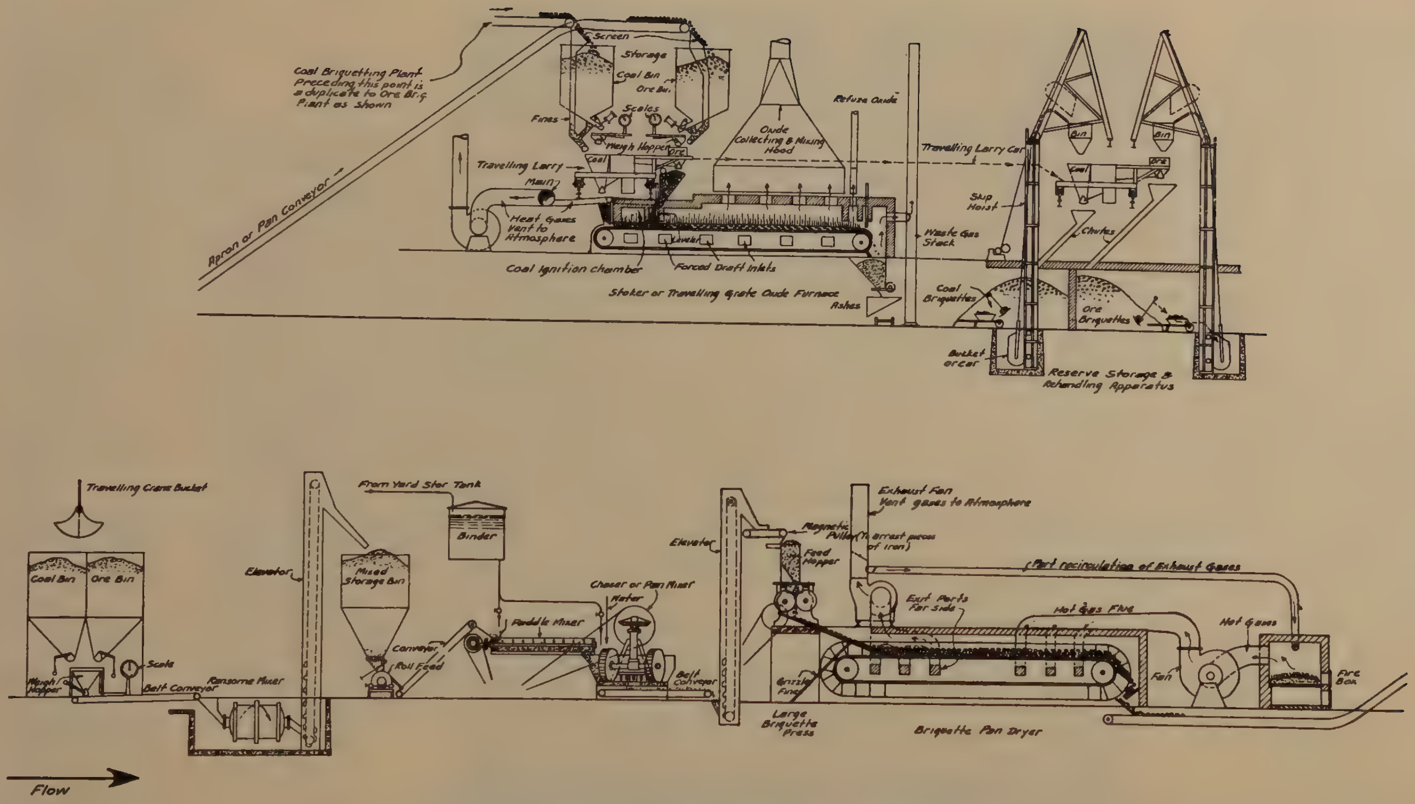


FIG. 10.—FLOWSHEET OF MECHANIZED ZINC OXIDE PROCESS.

of zinc in addition to ore. The coal used is a low-grade, very fine-sized anthracite.

These raw materials are weighed out in large scale hopper. The weighing in this apparatus is the only batch operation in the entire process. The mix for the ore briquettes usually consists of 80 per cent zinc-bearing material and 20 per cent coal. From the weighing hopper the material is transferred to a feed bin, the bottom of which is equipped with a feed roll of which the discharging rate is controlled by an adjustable gate. The feed roll delivers the material to a belt conveyor, which carries it to an edge-runner or Chilean mill. Two of these mills are used in series. In the first mill the binder (waste sulphite liquor from the paper-pulp mills) is added and the moisture content of the mix roughly adjusted The mix is discharged through the floor of the first edge-runner and conveyed by belt to the second edge-runner. In the second edge-runner the moisture content of the charge is finally adjusted to produce a proper consistency for briquetting. The mix is then elevated to the briquette press, which is a conventional Belgian roll press. (Fig. 10.)

The briquettes are discharged upon a grizzly, which screens out any unbriquetted fines. The fines that pass through the grizzly are returned to the press; the briquettes are transferred to a basket drier. A counter-current stream of hot gas passes through the baskets of briquettes as they travel in an endless chain through the drier.

After drying, the binder has set so that each briquette is a hard, compact mass. The shape of the briquette resembles a small pillow, measuring 2 in. on a side and about 1½ in. through its thickest part. The briquettes are cooled as they are conveyed on a long pan conveyor to a large bin at the top of the furnace building.

The coal-briquetting plant is similar to the ore-briquetting plant, except that only one edge-runner is used and a rotary drier is provided ahead of the edge-runner to reduce the moisture content of the raw coal, which as taken from the stockpile is too wet to briquette. The raw material is the same low-grade anthracite coal that was used as an ingredient of the ore briquettes. The only materials used in compounding the mix for the coal briquettes are coal and waste sulphite liquor as binder.

The drying and conveying equipment for the coal briquettes is a duplicate of that provided for the ore briquettes.

Under the briquette-storage bin in the furnace building is a larry car equipped with scale hoppers, which weighs the briquettes and conveys them from the storage bin to the furnace.

The most recent development in this process, however, dispenses with all conveying and drying equipment for handling the briquettes, by placing the briquette press directly above the furnace, and by drying the briquettes with waste heat from the furnace. In consequence of the decreased handling of the briquettes, less binder is necessary in the ore briquette when this arrangement is adopted. This improvement saves much capital expense as well as the cost of drying and conveying the briquettes and decreases the expenditure for binder.

Operation of Traveling-grate Furnace

The grate used in the furnace is a traveling-grate stoker developed originally for firing steam boilers. It has been modified somewhat to adapt it for zinc oxide production, but its general construction has not been altered. The grate surface consists of a number of built-up units arranged in an endless chain driven by sprockets at each end of the flat surface. The grate bars are made of cast iron and are 12 ft. long. They are provided with a pin lock at each end by means of which they are fastened to supporting chains. Each of these bars is equipped with a set of malleable-iron castings called "dovetails," which are bolted over the entire length of the bar. These dovetails hold the cast-iron keys (so called because of their resemblance to piano keys) that form the bearing surface for the charge. The keys are cast with nubs on one side, so that when assembled the desired space is provided between adjoining keys for the passage of the forced draft.

In operation, the traveling grate traverses the tunnel-shaped firebrick furnace chamber (Fig. 11), passes over the sprockets at the rear and returns under the furnace to the front. At the front, or charge end, of the furnace, a hopper receives the coal briquettes and as the grate moves forward under this hopper it picks up a bed of coal briquettes. The depth of the bed is determined by the height of a water-cooled cast-iron leveler or gate, adjustable to a fraction of an inch by a pair of screw jacks outside the furnace wall. The normal depth of the coal bed is 6 to 6½ inches.

The grate then carries the bed of coal briquettes forward into the furnace. The first compartment of the furnace is a coal-ignition zone, consisting of a short hot section in which part of the fuel in the coal briquettes is burned to maintain a temperature of 1000° to 1050° C. The ignition of the coal briquettes is continuous, the incoming briquettes being ignited by the preceding burning briquettes.

The bed of incandescent coal briquettes is now carried by the grate under an ore hopper, which deposits a bed of ore briquettes of predetermined depth on top of the burning coal briquettes. The depth of the bed of ore briquettes is also regulated by a water-cooled cast-iron leveler similar to that used for controlling the depth of the bed of coal briquettes. The depth of the bed of ore briquettes is normally about 6 in. As the grate advances into the reduction zone, the charge carried by it is subjected to forced draft, and the reduction of the ore in the briquettes starts. Zinc vapor is driven off and passes out of the furnace. The charge traverses the reduction zone and, as the grate turns downward to return to the front of the furnace, the clinker consisting of the residue of the charge from which the zinc has been expelled is dropped into waiting cars to be removed to the dump, or to other metallurgical furnaces for recovering values that may be present.

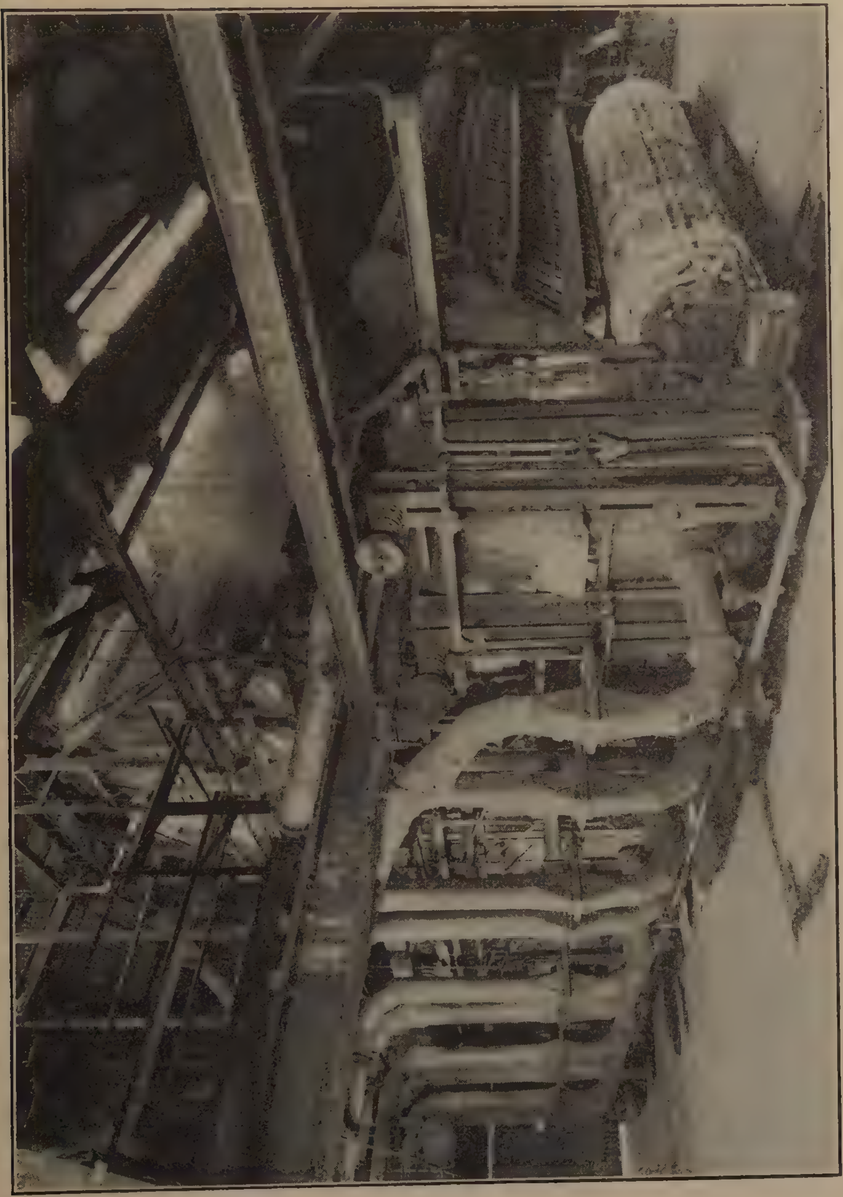


FIG. 11.—MECHANICAL ZINC OXIDE FURNACE.

Adhesion of the charge to the side walls of the furnace is prevented by constructing the side walls of water-cooled plates.

The forced draft supplied from beneath the grate in the reaction zone is controlled by means of 10 windboxes, each provided with an independent damper, so that the intensity of the draft forced through the charge can be gradually increased as the charge advances through the furnace; the wind boxes also prevent short-circuiting of the draft.

The coal-ignition zone, the arch over the zone where active reduction occurs, and the offtake flue for the finished product are equipped with thermocouples for registering the temperatures prevailing at these points. This brings the entire process under the control of the operator.

The zinc vapor passes through the arch openings in the roof of the reduction chamber, into a combustion chamber or chambers where the oxidation of the zinc vapor can be controlled.

The collecting system and its connection with the combustion chamber are substantially the same as in the Wetherill-grate furnace practice already described.

This mechanical furnace obviously does away with the hot and onerous labor conditions of the old process and for its operation requires attendance rather than labor. The output per furnace or per square foot of grate surface is increased tremendously and the result is lower operating and investment cost per pound of product. The quality of the product is also under better control, resulting not only in better quality but in better control of the many types of product now required by the consuming trade.

Treatment of Residues from Electrolysis of Zinc and of Lead-furnace Slags in Ash-fusion Gas Producers*

By J. Van Oirbeek†

The ash-fusion gas producer, blown with air preheated to a high temperature, was perfected by the Société des Houillères de Saint-Etienne during the years 1920 to 1925, for the treatment of a mixture of ashy fuel and limestone. The temperature, about 1800° C., obtained by using hot air in running the producer, ensures the fusion of all the slag and the transformation into carbon monoxide of every particle of carbon contained in the materials treated.

During recent years this apparatus has been used for the treatment of ores and complex residues containing such volatile metals as zinc, lead and tin on the one hand, and on the other such metals as copper, silver, gold, nickel and cobalt, which can be concentrated in a matte tapped with the slag at the base of the apparatus.

This paper considers three interesting applications of the ash-fusion producer, chosen as examples:

1. The treatment of the residues from the electrolysis of zinc.
2. The treatment of lead-furnace slags.
3. The treatment of tin-bearing residues.

The apparatus described has been in operation for more than seven years at the Viviez works of the Société de la Vieille-Montagne. Other installations are derived from it, and are almost identical in principle.

THE VIVIEZ APPARATUS

The apparatus consists of an oval shaft furnace with a cross section of 6.50 sq.m. at the tuyeres. The casing is wetted externally by trickling water. The dimensions of the producer are 1.65 by 4.25 m. The cross section is constant to a height of 3 m., then flares slightly up to the gas outlet. The total height from the tuyeres to the charging mouth is ±5.50 meters.

This apparatus is topped by a charging chamber that is operated hydraulically. On both sides rises one gas outlet, 1 m. in diameter, ending in a dust hopper. The whole is designed for easy cleaning of the upper parts, where incrustations have a tendency to collect.

---

* This paper was presented at Session VII of the Congrès International des Mines, de la Métallurgie et de la Géologie Appliquée, October, 1935. The translation is published by permission of the President of the Congress.

† Engineer, Chief of Engineering Service of the Société de la Vieille-Montagne, Paris, France.

There are 11 water-cooled bronze tuyeres, 100 mm. in diameter, five on each face and one opposite the taphole.

The crucible fills 30 to 40 cm. below the tuyeres, with a slant toward the taphole.

The shaft is of 30-mm. sheet steel with a refractory lining and external water-cooling up to 2.50 m. above the tuyeres. Charging is done with a Staehler bucket.

Air Preheaters.—The hot air is supplied to the tuyeres by a fan having a capacity of 11,000 cu.m. per hour. It is heated in two groups of Philipon heaters, which can work separately or in parallel and can heat 11,000 cu.m. of gas to 500° C. They consume 15 to 18 per cent of the gas produced by the producer. The blast pressure at the tuyeres is about 1.500 m. (about 59 in.) of water.

In general, the materials treated in the cupola are either charged in lumps or agglomerated into briquettes, with or without the addition of carbon. A certain percentage of flux may be added to the charge.

Treatment of the charged material gives: the products of volatilization (zinc, lead and tin oxides); the combustible gas which, after supplying the heaters, can be used in various ways; a matte with a basis of iron sulphide in which the copper, silver, gold, nickel and cobalt are concentrated; and a slag.

The products of volatilization are sent to an electric dust remover of the Cottrell type or are condensed by a wet process. At Viviez, the latter method has been adopted, the following apparatus being used: (1) a vacuum scrubber, 10 m. high and 2.50 m. in diameter, receiving through a sprayer an hourly supply of 30 cu.m. of water; (2) a scrubber with screens, 20 m. high and 3.30 m. in diameter; (3) a Theisen, which reduces solids to some milligrams per cubic meter of gas; a figure compatible with its final use in a gas engine.

The gas, after leaving the Theisen, is dried and sent to the apparatus using it.

The wash waters from the various wet-condensation devices are combined in a settler from which the slimes are extracted and carried to a rotary filter; they are then sent to the room where they are to be treated.

Treating Residues from Electrolysis of Zinc

The electrolytic manufacture of zinc leaves residues from the lixiviation and purification of the solutions, which still contain relatively important proportions of various metals. When the geographic situation of the electrolytic plant permits, these residues are sent to a lead works where they are treated in a water jacket, as at the great electrolytic zinc plants of the United States and Canada (Trail).

The Viviez electrolytic zinc works is too far from a lead works to make it possible to consider shipping its by-products, which are poor in lead. For this reason treatment on the spot in the ash-fusion producer has been considered.

The electrolytic residues at Viviez have approximately the following contents, which vary somewhat with the ores treated: Zn, 18 to 23 per cent; Pb, 1 to 6; Cu, 0.5 to 1.5; Ag, 200 to 500 and Au, 0.5 to 1.5 grams per metric ton; Cd, 0.2 to 0.5 per cent; As and Sb, 0.20 to 0.30 per cent.

These residues contain also the following substances, which come from the gangue of the ore: SiO_2, 2 to 6 per cent; Al_2O_3, 2 to 8; CaO 1 to 4; MgO, 1 to 1.5; MnO, 1 to 2; Fe_2O_3, 20 to 38; S, 5 to 8, mostly in the form of sulphate.

Briquetting.—The vacuum filters of the electrolytic plant deliver residues containing 35 per cent of moisture; they are carried through steel pipes by a screw, then by air compressed to 4 kg., to a stock bin placed at the head of a drying tube. The coke dust and returned dust are added before drying.

The drying tube is 2.70 m. in diameter and 18 m. long. Its inclination is 4 per cent and the speed is 2 r.p.m. It is partitioned to increase its efficiency.

The gas, either supplied by burning the gas from the cupola or from a mechanical roasting furnace, circulates in the same direction as the slime, in order to avoid too great clogging. This is, in addition, broken up by automatic beating.

The capacity of the tube is ±200 tons per day. The material leaves at 150° C., still containing 5 to 6 per cent of moisture. It is stored in two cement hoppers. The gas from the combustion undergoes a dry dust removal in a cyclone and hoppers, and then a wet dust removal in a scrubber.

The product, slightly moistened in a rapid stirrer, is compressed by Brück rotary presses. A pressure of 400 kg. per sq. cm. has been found sufficient. The briquettes are 130 mm. in diameter, 80 mm. high, and weigh 1600 kg. A press produces 40 briquettes per minute. They are handled mechanically to a tunnel 40 m. long, where they are dried by a counter current of burnt gas from the air heaters. This drying is then advantageously succeeded by storage in the open air for three or four days.

Composition of Charge.—The Staehler bucket charger is fed from the hoppers where the various components of the charge (briquettes, coke, shale, limestone) have been collected. A bucket containing 1200 kg. of briquettes and the additional products is charged four or five times per hour.

In the procedure carried out at Viviez, excess of carbon is avoided, which would lead to too hot working and in consequence to the formation of metallic iron, which is not desirable when the content of precious metals is high.

The fluxes added vary with the content of the residues. If these have a calcareous and siliceous gangue, the operation is much easier. Silica is introduced in the form of shales, coal-mining refuse, from which the carbon and volatile matter are thus recovered.

The briquettes should contain the highest possible percentage of carbon. In practice, this rarely exceeds 16 to 17 per cent. In order to complete the necessary 25 per cent, metallurgical coke is added.

The apparatus can treat a daily tonnage of 100 tons of residues in 160 to 180 tons of charge.

Products of Fusion.—Tapping is intermittent. It is done in cast-iron ladles, four times per hour.

Slag.—An endeavor is made to obtain a slag containing the maximum of iron compatible with a minimum of zinc. The density should be such that decantation from the matte is rapid enough to permit granulation of the slag. Experience has shown that favorable conditions are nearly realized by a slag containing 30 to 34 per cent SiO_2, 18 to 24 per cent CaO and 18 to 20 per cent FeO.

Matte.—The production of matte is a function of the amount of iron in the mixture. Part of the iron is present as FeS, the remainder as Fe. The sulphur content is regularly 24 to 26 per cent. A normal concentration of the metals, silver and copper, is 4 to 5, referred to the electrolytic residue, which gives approximately the following averages: Fe, 55 per cent; Cu, 6 to 7 per cent; Ag, 1800 to 2000 grams per metric ton; Au, 5 grams per metric ton; S, 25 per cent.

Certain elements that constitute the impurities of the electrolysis of zinc are eliminated with the matte; i.e., cobalt, nickel, manganese, arsenic and antimony.

Gas and Products of Volatilization.—The gas produced by the apparatus approximates blast-furnace gas. It contains ±10 to 12 per cent CO_2 and 23 to 25 per cent CO. Taking into consideration the hydrogen and hydrocarbons, it gives approximately 800 cal. per cubic meter.

For an operation corresponding to ±90 tons of residues per day, there is a production of ±240,000 cu.m. of gas. The heat balance shows that 55 per cent of the calories brought into action is utilized for the metallurgical operation and the production of the gas required to heat the air. The remaining 45 per cent of the calories is available for other uses.

The outgoing gas from the apparatus passes through a hopper for catching coarse dust, from which it issues at ±400° C., with a content of products of volatilization of 80 to 100 grams per cubic meter.

After condensation by wet methods, a concentrate containing 70 per cent of metal, zinc and lead, is finally obtained.

Table 1 gives, together with the analysis of the materials charged, the details of the products recovered in an operation treating 1300 tons of briquettes.

The recoveries of metals in this operation were: Zn, 88 per cent; Pb, 85; Cu, 93; Ag, 94; Au, 95 per cent.

Utilization of Cupola Products.—The zinc and lead concentrate returns to the electrolytic cycle where, after bringing the zinc and cadmium into solution, a lead sulphate with 50 per cent Pb is obtained, which is sold to lead works.

TABLE 1.—*Material Balance Sheet of an Actual Run of the Viviez Ash-fusion Producer (Dry Weights)*

	Materials Charged[a]					Products Recovered[a]		
	Briquettes, 1300 Tons		Large Coke, 350 Tons	Limestone, 180 Tons	Siliceous Flux, 80 Tons	Slag, 600 Tons	Volatilized Dust, 280 Tons	Matte, 240 Tons
	Residues, 1000 Tons	Coke Dust, 230 Tons						
Zn, per cent	20.3					1.6	63	3.9
S, per cent	8					0.1	7.4	25.4
SiO_2, per cent	5.5	9.3	9.3		64.2	28.2	2.3	
FeO, per cent	24.3	2.5	2.5		4.3	18.4		Fe = 56
Al_2O_3, per cent	6.5	4.0	4.9		13.7	17.9		
MgO, per cent	0.5					0.9		
CaO, per cent	2.7	1.0	1.0	52	0.55	21.7		
BaO, per cent	0.9					1.5		
Pb, per cent	3.9					0.7	11.4	1.5
Cu, per cent	2.1					0.10	0.19	8.3
Ag, grams per metric ton	479					40		1890
C, per cent		78	80					

[a] Dust recharged, 70 tons; dust recovered, 70 tons.

Because of its composition, the matte is a product of great interest to lead and copper works that can utilize all its elements; unfortunately these works are situated abroad and the cost of transportation from Viviez is high.

Completer valorization at Viviez of the metals in the matte is contemplated through a chemical operation in a special plant which will begin operation next October, using the following method:

1. An attack on the matte by the acid liquor of the electrolytic vats, containing 120 grams of free acid per liter, which will give a liquid containing iron sulphate and hydrogen sulphide. The iron sulphate will be

partly used to purify the electrolytic zinc solutions and partly sold as crystallized sulphate for agricultural use.

2. The residue from this first treatment will be dried and heated, and dissolved in 50° Bé. sulphuric acid. A mixture of iron and copper sulphates containing the gold and silver will be obtained, and SO_2 gas which will enter into the sulphuric acid manufacture.

From the solution, after the copper is removed, crystallized iron sulphate will be extracted. The copper sulphide, after roasting, dissolving and crystallizing, will be transformed into marketable copper sulphate.

3. The hydrogen sulphide produced in the first operation will be transformed into sulphur by catalytic oxidation in a special furnace.

Treating Lead-furnace Slags

The Baelen works, also belonging to the Société de la Vieille-Montagne, have been supplied with three cupolas which, by treating lead-furnace slags, supply annually an amount of zinc oxide sufficient to feed an electrolytic zinc works with an annual capacity of 6000 to 8000 tons.

The material charged at Baelen is either in the form of lump slag, when it comes directly from the lead works, or in the form of granulated slag, large stocks of which have been accumulated during many years. In the latter case it is formed into briquettes with sulphuric acid as binder.

Average results of running the Baelen cupolas are as follows:

Materials Charged.—The lump slag corresponds approximately to the following analysis: Zn, 8.60 per cent; Pb, 2.25; Cu, 0.40; Ag, 35 grams per metric ton; SiO_2, 34 per cent; FeO, 30; CaO, 11.50 per cent.

The coke used contains: ash, ±10 per cent; volatile matter, ±9.25 per cent. As a sample, an average analysis of the coke ash is: SiO_2, 63 per cent; Fe_2O_3, 12.50; Mn_3O_4, 0.25; Al_2O_3, 18.50; CaO, 2.80; MgO, 1.50.

The composition of the charge is: slag, 1000 tons (20 per cent briquettes and 80 per cent lump); coke, 449 tons; proportion of fixed carbon, ±25 per cent; amount of slag treated daily by the apparatus in normal operation, ±190 tons.

The products obtained, per ton of slag treated, are: oxides, 148 kg.; matte, 115 kg.; slag, 850 kg. Analyses of these products are given in Table 2. Approximate analysis of the gas is: CO, 26 to 29 per cent; H_2, 2 to 3; CH_4, 0.2 to 0.6; CO_2, 4 to 6; calorific power of the gas, 930 cal. per cubic meter.

Average recoveries (calculated on a period of six months) are: zinc, approximately 90.5 per cent; lead, approximately 98; copper, approximately 95; silver, approximately 83 per cent; tin, undetermined.

Total amount of gas produced per ton of slag is 1980 cu.m.; amount of gas available per ton of slag, after feeding the heaters, 1700 cu.m. Corresponding number of kilowatt-hours (per ton of slag) is 385; number of kilowatt-hours necessary to deposit electrolytically the zinc contained in the oxide obtained by treating one ton of slag, 296.

Utilization of Products Obtained.—The electrolytic works not being ready yet to operate, the oxides are sent to a zinc smelter, in spite of their large content of lead.

The matte is sold or used at the Baelen lead works, with an enrichment in view which will permit recovery of the copper.

TABLE 2.—*Approximate Analyses of Products*

	Analysis of Crude Oxides	Analysis of Oxides, Calcined in Rotary Furnace	Analysis of Matte	Analysis of Slag
Zn, per cent	51.50	51.40	1.20	1.50
Pb, per cent	16.00	15.80	2.90[a]	0.60
Cu, per cent	0.05		5.50	0.15
Fe, per cent			58	23.00
Ag, grams per metric ton	35		270	
SiO_2, per cent	5.00			33.00
Al_2O_3, per cent	4.00			
C, per cent	3.50			
S, per cent	3.00	total 2.40 sulphate 1.50	24	2.50
Sn, per cent	0.03			
Sb, per cent	0.01			
CaO, per cent				15.00

[a] By dry method.

The number of kilowatt-hours that can be produced from the gas will be amply sufficient for the electrolysis of the oxides obtained at the outlet of the apparatus. The "cupola-power plant-electrolysis" combination can thus constitute an independent cycle. But this gas, being a choice fuel, has been by preference reserved for the little, intermittently worked furnaces scattered through the rest of the works, and will continue to be used in this way when electrolysis has commenced. Use of the gas in these furnaces has made it possible, in fact, to realize very interesting calorific efficiencies corresponding to considerable economies in the cost of heating.

Up to the present, even at the lowest metal prices, the "cupola-power plant" combination at Baelen has always shown a profit, thanks to the good working of the whole installation.

TREATING STANNIFEROUS RESIDUES

The Société Française des Métaux et Alliages Blancs has at its disposal a stock of residues from the passage of stanniferous material through a water-jacket lead furnace.

An ash-fusion producer is now being built at its Saint-Denis works with a view to a treatment of these residues, which will permit recovery of the tin and other metals that they contain.

There the question is one of an apparatus with smaller dimensions than those described above. It is composed of a shell of special steel, circular in form, carrying at its base a series of six water-cooled bronze tuyeres.

The gas emerging from the cupola will pass into an aerial cooler. Electrical dust removal in a Cottrell will be adopted here; the volatilized dust will settle on the bottom of the cooler and the Cottrell, from whence it will be collected.

Materials Charged.—The slag occurs in the form of crushed lumps and corresponds approximately to the following analysis: Zn, 4 per cent; Pb, 1.8; Cu, 0.5; Sn, 2; SiO_2, 20; Al_2O_3, 5; CaO, 5; Fe, 53.

In the course of a test made with an apparatus of small size, charges composed about as follows were introduced into the apparatus: coke, 30 per cent; slag, 55 per cent; gypsum, 15 per cent. An efficiency of volatilization of the tin of the order of 90 per cent was obtained.

In the contemplated plant, the volatilized oxides, containing zinc, lead and tin, will be treated electrolytically with a view to recovering the tin.

The slag will no doubt have a small content of zinc, lead and tin (content of tin, about 0.30 per cent).

As for the gas, a fraction of ±15 per cent will be utilized in the cupola heaters, and the remainder for heating metallurgical furnaces.

The apparatus of the Société Française des Métaux et Alliages Blancs will not be put in operation until August or September. The present communication having been written in June, 1935, can therefore not contain precise data upon the results obtained.

CONCLUSION

In this communication we have set forth three applications, chosen as examples, of the ash-fusion producer for the treatment of the residues from metallurgical works.

What characterizes this process is its great flexibility, which makes it possible, especially by varying the blast temperature, to treat the most diverse materials.

In the course of several years of operation, very heterogeneous residues from the electrolysis of zinc have been passed through the cupola at Viviez, for the ores treated are of great variety; their gangue, on the other hand, is often difficult to smelt. Nevertheless, the apparatus always functions excellently. At present metal prices, the value of the matte alone is greater than the cost of treating the residues.

When it is a question of poorer metals, such as the lead slags of Baelen, it is necessary, in order for the cupola treatment to be profitable at present low metal prices, to reduce the cost of labor as much as possible by using apparatus of great capacity. It is, in addition, indispensable to have, as at Baelen, good use for the gas.

In conclusion, the use of the ash-fusion producer blown with air heated to a high temperature can render great service to a number of industries that seek to valorize residues which they have theretofore not been able to utilize.

Det Norske Zinkkompani, Norwegian filial society of the Compagnie Royale Asturienne des Mines, has decided to adopt, at its plant at Eitrheim, the ash-fusion gas producer for the treatment of residues from electrolysis of zinc.

The Waelz Process

By William E. Harris*

Time and experience have demonstrated that by means of the Waelz process zinc, lead, cadmium, arsenic, antimony, bismuth and tin can be volatilized satisfactorily. In this way difficult gold ores are being treated to allow for the recovery of the precious metal. Iron ore containing zinc is being treated to remove the zinc and recover the iron. In Germany, thallium is being recovered in commercial quantities from the zinc oxide fume; indium, germanium and gallium are also concentrated to a degree warranting recovery, even though these rare metals are only recognizable in the ore by means of the spectroscope. The physical, chemical or mineralogical condition of the raw material affects very little the applicability of the process.

The name Waelz is derived from the German word *Waelzen,* meaning a "trundling motion," which very aptly describes the movement of the charge through the slowly rotating kiln.

The recovery of zinc and lead by volatilization in a rotary kiln has its origin in a process patented in 1910 by Edward Dedolph, of British Columbia. The Dedolph patent was taken over by the Metallgesellschaft of Frankfurt-on-Main, Germany, which in cooperation with the Griesheim-Elektron, now a part of a large industrial combine, introduced certain improvements (Ohlmer, Specketer patents), but without bringing the process to a state suitable for large-scale operations. The war temporarily stopped all work on the process, and it was not until after the war that the Krupp Grusonwerk, of Magdeburg-Buckau, Germany, quite independently of the Metallgesellschaft, instituted research work in this field of metallurgy, which in 1923 led to the Waelz process proper. The Krupp Grusonwerk and the Metallgesellschaft A.G. later on collaborated, and by their joint efforts further developed and perfected the Waelz process, which they are marketing together as "Waelz-Gemeinschaft."

The process is capable of treating a varied type of material; for instance, oxidized and sulphide zinc ores, calamine (zinc carbonate ore) waste dumps, jig tailings, jig slimes, table concentrate slimes, brass ashes, zinc-bearing iron ores (where the iron sinter is the real objective and the zinc oxide a by-product), electrolytic-zinc leach residues, zinc muffle residues and works sweepings, lead-furnace slags, tin ores and slags, anti-

---

Manuscript received at the office of the Institute July 28, 1936.

* Consulting Chemical and Metallurgical Engineer, Ottawa, Ont., Canada.

mony and arsenical gold ores (where, of course, the gold is the real objective). The process has also been applied in the treatment of complex ores containing zinc, copper, lead and precious metals.

OPERATION AND APPARATUS

The Waelz process is very simple and can be operated by unskilled labor, under supervision, as efficiently as the blast furnace. It has many aspects that should appeal to the metallurgist, especially the hydrometallurgist. There is no necessity for controlling roasting conditions, as ferrites, ferrates, sweet roast and sulphate roast are all easily reduced in the kiln. If any roasting is required, it is merely to reduce sulphur to a limit that will allow for easy absorption or "locking up" in the charge; not to eliminate it altogether. The Waelz process can easily handle 15 to 20 per cent sulphur without changing the usual procedure. Electrolytic leach residues need not be dried, for the process will treat slimes running 40 per cent moisture without any preliminary drying. The leach residue is simply mixed with the required quantity of coke and fed to the kiln.

The plant consists of three divisions: (1) preparation and mixing of charge, (2) the kiln, (3) collection and disposal of products.

The charge need not be finely ground (⅛ mesh is an ideal size), but fine concentrates, dust, slurries, can all be used without drying or sintering. The ore and coke are carefully apportioned before being put into the mixer. The coke can be gas or metallurgical coke, breeze, anthracite dust, or even waste ashes containing coke. The quantity of coke varies according to the nature of the ore and of the coke itself.

At some plants where calamine waste has been treated, the coke added has been as low as 10 to 12 per cent. At others, owing to low melting point or the difficultly reducible nature of the charge, as much as 30 per cent and in exceptional cases up to 40 per cent has been used. The quantity usually varies between 20 and 35 parts to every 100 parts of ore, the percentage of coke in the actual charge being in the neighborhood of 20 to 25 per cent. To give examples: With a raw material consisting of calamine slimes averaging 7.5 per cent Zn, 2 per cent Pb, 12.5 per cent Fe and 30 to 40 per cent moisture, the charge going to the kiln consisted of 76.25 per cent slimes and 23.75 per cent coke. On a roasted sulphide ore running 37.5 per cent Zn, 7.8 per cent Cu, 1.03 per cent Pb, 24.1 per cent Fe, 5.5 per cent S, the charge consisted of 75 per cent ore and 25 per cent coke. On a fusible lead-smelter slag running 20 per cent Zn, 1.5 per cent Pb, 1.5 per cent Cu, 7.0 per cent S, 36.0 per cent FeO, the charge consisted of between 72 to 75 per cent ore to 28 to 25 per cent coke, the kiln operating under "self-burning" conditions; that is to say, practically without the use of any auxiliary heating. The coke is given "dry as coke," although often its moisture ran as high as 15 to 20 per cent when added to the charge. Each ore must be studied separately and the charge arranged to meet its peculiarities.

The apportioning of ore and coke for the charge is done by any of the ordinary weighing devices, though in larger installations automatic weighers are used, of course. The weighed quantities are fed into a mixing unit. No special machinery is specified; sometimes a Chilean mill is used, sometimes an ordinary cement mixer. All that is necessary is to see that the charge is thoroughly mixed, as an intimate mixing of the charge leads to much better elimination of the volatilizable metals.

The mixed charge is conveyed to the kiln feeder by a mechanical conveyor, usually a belt conveyor. The charging of the kiln calls for no special machinery. Experience has led the engineers to revert to the simple inclined chutes, for though these cut down the effective area of the kiln at the feed end, at the same time they cut out much of the unnecessary air admitted by chargers of the shaking and revolving type. One plant had the feeding device built into the walls of the kiln, so that the charge was fed into a spiral and thence into the kiln, which obviated the backward building up of the charge and cut down the air admission, but the cost of the system outweighed the advantages, especially as the simple chutes are satisfactory.

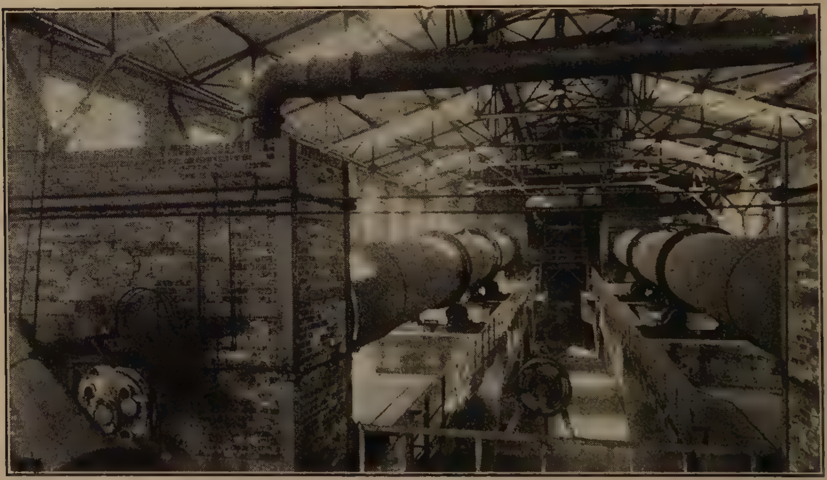


FIG. 1.—WAELZ KILNS AT BEUTHEN, GERMANY.

The kiln consists of a long, horizontally inclined cylinder (Fig. 1) made of a steel plate outer shell lined with firebrick. The slope varies from 1 to 6 per cent of the kiln length; the usual variation is between 2 and 4 per cent. Kilns vary in size from 40 ft. long and 6 ft. in diameter to 160 ft. long and 12 ft. in diameter.

The kilns usually are supported on bearings (Fig. 2) running on rollers, and are driven direct or by belt drive through a large toothed wheel that forms a part of the kiln shell. The belt drive is the better because it tends to take up unequal strains caused by the shifting of the center of gravity of the kiln and charge due to the formation of accretions inside the kiln. Variable-speed direct-current motors are used to drive the kilns, while alternating current is used for all other purposes. If the current fails, the kiln can be rotated by hand, to prevent any possible damage to lining or shell by the hot, stationary charge.

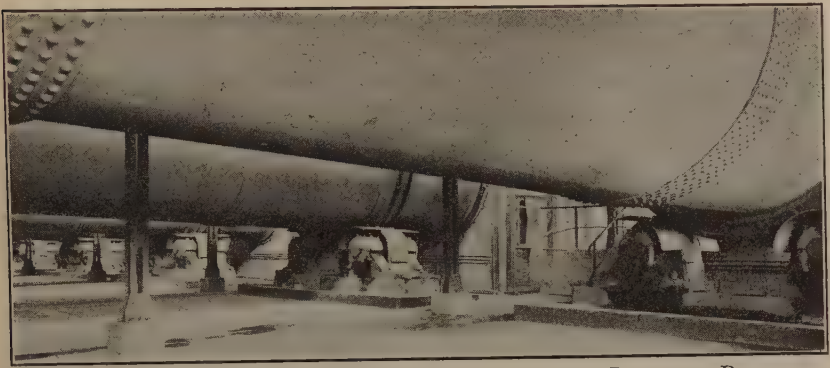


Fig. 2.—Supporting bearings under Waelz kilns at Brzeziny, Poland.

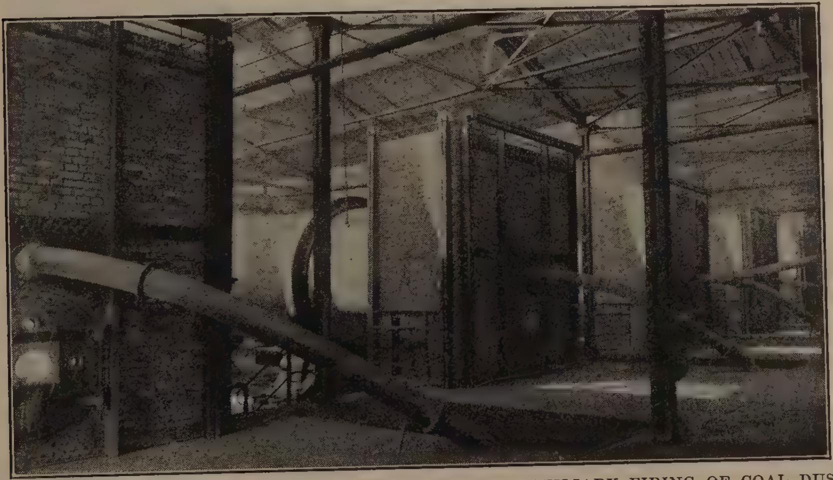


Fig. 3.—Observation platform, with pipe for auxiliary firing of coal dust, Brezeziny, Poland.

An observation platform (Fig. 3) is built at the discharge end of the kiln. The various control instruments are situated on this platform and the auxilary heating unit is fitted to and operated from it.

The gas flow (between 35 and 50 cu. ft. per second) is controlled by a fan situated beyond the fume-collecting plant, so that the whole system is under an induced draft. The temperature of the kiln is difficult to measure. By means of optical pyrometers, temperatures of 1120° to 1200° C. have been recorded in the kiln. The exit gases vary between 500° and 600° C., a great deal of the heat being absorbed by the incoming charge and in evaporating moisture.

The clinker from the kiln falls either into a dump car (Fig. 4) or onto a traveling belt, which conveys it to a dump car.

On a large kiln from two to six men per shift are employed. Power consumption does not exceed 25 to 30 hp. per kiln for the largest kilns.

The gases, fume and dust leave the kiln from the upper (feed) end and pass through a series of settlers and cyclone collectors where the dust is removed. The type of settler varies considerably. As the dust particles are so much heavier than the zinc fume a simple settling arrangement is efficient. At some plants it is merely a series of V's in a long pipe line, the heavier dust collecting at the bottom of the V's, where arrangements are made for its removal and return to the mixing house. The actual dust losses are negligible, as the dust collected, amounting to about 3 to 4 per cent of the charge, is returned to the mixer and reincluded in the charge.

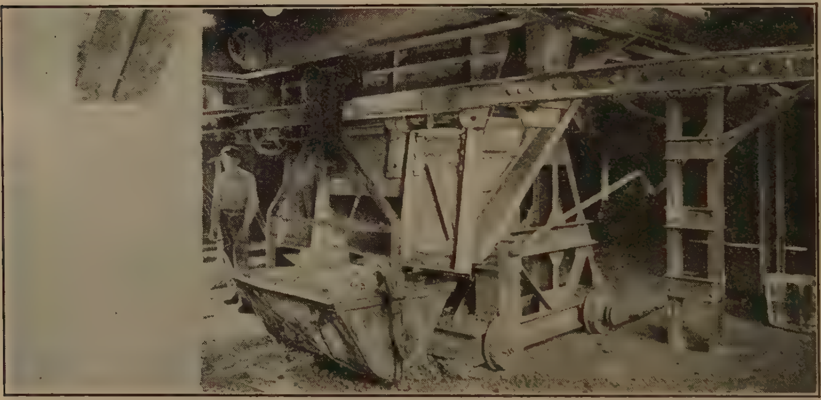


Fig. 4.—Dump car at discharge chute, La Calamine, Belgium.

In some kilns the cross section has been cut down by the insertion of metals "ribs" to impede and choke down the draft. In all plants where these have been installed there has been a marked decrease in the flue dust and a corresponding increase in the zinc content of the recovered oxide.

At another plant enlarging the diameter of the kiln at the charging end, by thinning down the brickwork, brought about a better preheating of the ore, owing, no doubt, to the decreased velocity of the exit gases, which also lessened dust formation.

The fume and combustion gases, if not sufficiently cooled in their passage through the settling plant, are cooled in pipes (Fig. 5) sprayed with water, to about 200° C., and then passed on to either baghouse or electrical precipitator of the Cottrell type.

Reactions Inside the Kiln

The charge, which takes about 2 hr. to pass through the kiln, meets the hot gases flowing in the opposite direction. The moisture is evaporated, the charge absorbs heat, so that it reaches the temperature required for the reduction of the zinc oxide in less than one-fifth of the length of the kiln. This absorption of heat is greatly facilitated by the constantly changing surface of the tumbling charge, and to a small extent by the radiation from the kiln lining. The reduction and volatilization occur uniformly over 80 per cent of the length of the kiln; depending, of course, on the speed of rotation and quantity of material charged (Fig. 6).

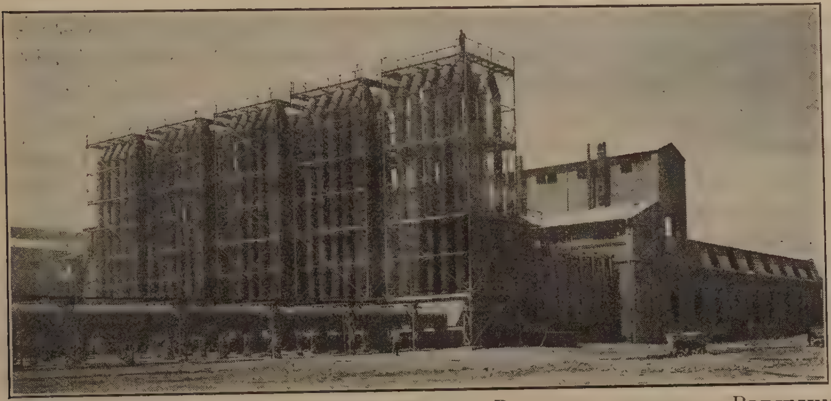


FIG. 5.—COOLING PIPES FOR ZINC OXIDE FUME. BAGHOUSE AT RIGHT. BREZEZINY, POLAND.

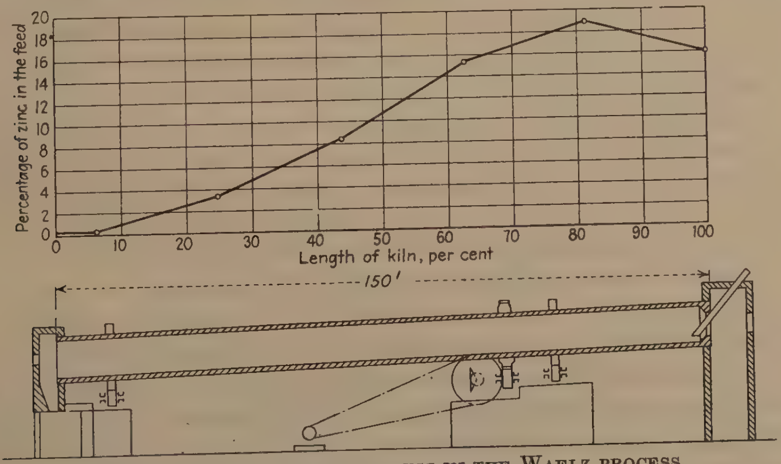


FIG. 6.—VOLATILIZATION OF ZINC IN THE WAELZ PROCESS.

The reduction, volatilization and reoxidation of the zinc proceeds along the following lines:

$$ZnO + C = CO + Zn \text{ (vapor)} \qquad [1]$$
$$Zn \text{ (vapor)} + CO + O_2 = ZnO + CO_2 \qquad [2]$$
$$C + O_2 = CO_2 \qquad [3]$$

By combining equations 1 and 2 there will result as the total of the reactions taking place at any one particular section of the kiln, inside and outside the charge, the simple exothermic burning of the carbon, equation 3; the carbon of the charge being burnt to CO_2 with the greatest possible evolution of heat. The reduction of the zinc in the charge being endothermic, and the oxidation of the zinc vapor just above the charge being exothermic, there is a balanced heat reaction over the entire reduction zone of the kiln. The chemical action itself does not require surplus fuel for its maintenance; any surplus fuel added is used only to maintain the temperature of the kiln against losses in flue gases and kiln radiation.

In treating a sulphide material such as a blende, the Waelz operation is simplified if the ore is subjected to a preliminary roasting to reduce the sulphur to about 10 per cent. It is not absolutely necessary but it helps in many ways, particularly because a high sulphur content in the charge leads to slagging and the production of a matte that has a low melting point. The desulphurizing can be carried out in any form of roaster. Recent developments have made it possible to use a circular type of Dwight-Lloyd machine. This machine has proved very efficient, is cheaper to build and operate, and obviates a great deal of dusting so common to most roasting furnaces, especially those of the multihearth mechanical type.

If for any reason a straight sulphide must be treated without a preliminary roast, crushed limestone or lime is added to the charge to "fix" the sulphur, the reaction being:

$$ZnS + CaO + C = Zn \text{ (vapor)} + CaS + CO$$
$$Zn \text{ (vapor)} + CO + O_2 = ZnO + CO_2$$

The conditions are the same as those given for the treatment of an oxidized material. The reactions develop the same amount of heat.

Materials containing up to 20 per cent sulphur can be treated without preliminary roasting. Naturally, the question of the presence of SO_2 in the flue gases is an important one, but should any SO_2 be liberated, it would be immediately oxidized to SO_3, which in turn would attack the metallic oxides present and form sulphates. The highest SO_2 ever recorded as found in flue gases in a Waelz kiln ran 0.01 per cent. The sulphates in the Waelz oxides always run under 1.5 per cent.

The successful operation of the Waelz process largely depends on keeping the charge "dry"—that is, metallurgically dry; free from slagging. It also lies in the fact that the reducing action is carried on for a comparatively long period. The maximum temperature is limited by the softening point of the charge, which for ores of the nature usually treated by the process is only a little above the temperature required for the reduction and volatilization. As soon as the charge slags and becomes fluid, the fuel separates out and reduction stops. The factor influencing the completeness of the reaction is the length of time it lasts. As previously stated, the reduction zone of the Waelz kiln is about 80 per cent of its length, which, coupled with the fact that the charge takes about 2 hr. to pass through the kiln, accounts for the very high efficiency of the process. This also explains why the volatilization attempted by Dedolph under his patent was not crowned with success, for he charged the ore and fuel into the kiln and subjected them to direct heating by means of a flame in order to smelt the charge. He did not realize that by making the charge fluid he defeated his object, in that the reducing agent, the coke and coal, had a tendency to float on the molten charge and thereby cut short the time of reaction, which must of necessity therefore have been incomplete.

The reactions may easily be observed in the kiln. In the zone of volatilization, small flames, colored with the peculiar bluish green of burning zinc, appear immediately above the charge, the bulk of the kiln being filled with an incandescence that dazzles the eyes. It is an interesting, and to the uninitiated an awe-inspiring sight, to look into the kiln and observe the movement of the charge. Here, for instance, is a large lump, heated and highly colored almost to incandescence. It slowly climbs the side of the kiln until its weight overcomes the pull of rotation; then it falls, scattering sparks, to again climb the side. Each time it falls, it falls nearer the discharge, until at last it topples over a ridge of cooled charge that forms at the discharge end of the kiln, out onto the clinker conveyor, which carries it through water for cooling and so to a dump car. The reactions are considerable, for the heated mass on being submerged creates volumes of steam, and also brings about many violent chemical changes that release inflammable gases, which ignite with sharp cracklings and small detonations as they bubble to the surface. As you look into the kiln you can see the "fume" being formed and drawn away by the flow of gases, the reaction lessening as the discharge end is approached, the bluish green flames being at last replaced by the yellowish one of burning fuel. This yellow flame is a good indication of the completion of the volatilization of the zinc.

Therefore, the essential feature of the process lies in the fact that the reducing and oxidizing zones do not follow each other but are actually superimposed over the whole length of the reaction zone, from which it follows that the amount of heat consumed by the chemical reactions taking place at any particular portion of the kiln is balanced by the heat developed by the formation of the oxide, so that the heat losses in the waste gases, radiation and the like, must be balanced by the coke or coal added to the charge. The main heat losses are in the waste gases. These gases have an average composition of from 0 to 1 per cent O, 0 to 2 per cent CO, 18 to 28 per cent CO_2, the latter depending upon the quantity of carbonates in the charge. The solid content of the gases going from the Waelz kiln varies considerably according to the nature and fineness of the material to be treated. On one kiln where measurements were made over an extended period, it was found that the gases leaving the kiln carried 1 to 3 grams per cubic foot (at standard conditions; i.e., 0° C). Some plants have installed waste-heat boilers to utilize the heat in these gases. The steam so generated is sold to other departments of the works and the money is credited to the Waelz plant, materially reducing the charges against it.

Practical experience has shown that the heat developed by the reactions inside the kiln are sufficient to maintain the temperature required for the reduction of the zinc; in fact, the heat developed is often greater than is required, and to maintain a balance it is necessary to introduce cold air until the desired conditions are obtained. On the other hand, there may be a cooling off, especially at the discharge end, which is open to the air, where the inflowing cold air takes up a large proportion of the heat of that part of the kiln. This loss is made up whenever necessary by blowing in through suitable burners either powdered fuel or oil, or a mixture of the two, until the required temperature is reached and maintained. This auxilary heating is intermittent and often it is not used for long periods of time. Experience has also shown that this cooling of the discharge end does not materially affect the actual reduction zone, as the flame only preheats the incoming air and in this way helps to maintain the kiln temperature.

Accretions form one of the difficulties in the operation of a Waelz kiln, their formation and elimination being a matter of serious moment and study for the Waelz engineer. A basic ore favors ring formation, especially if it runs high in iron. An acid ore favors slagging, and the half-liquid method of operation. Accretions can be just small lumps clinging to the side of the kiln, or huge rings, which so reduce the diameter of the kiln as seriously to impede the movement of the charge. The main cause of accretions is unequal temperatures between the kiln lining and charge; a cold lining and hot charge, or a hot lining and a cold charge, are favorable to ring formation; the more nearly equal the temperatures of lining and charge, the less likelihood there is of ring formation. This condition could be more easily maintained by preheating the charge in a separate furnace, but experience has shown that the ring formations can in a large measure be controlled in the kiln itself, by intelligent operation of the mixing of the charge, rotation of kiln and rate of feed.

The operation of Waelz kilns over several years has proved that the best way to remove ring formations is either to vary draft conditions, or the rate of rotation of the kiln, whereby the zone of reaction can be moved either in front or behind the ring, promoting a loosening of the ring structure and causing it to collapse, or by adding additional coke, which tends to superheat the rings and so cause them to fall apart.

A ring formed near the discharge end can easily be broken up by means of a small flame, or by increasing the temperature of the kiln so that the slag holding it to the lining is softened and the ring can be pushed out either by hand or by the pressure of the charge. Incidentally, it should in fairness be stated that with the practical knowledge that comes with years of experience, "ring formation" does not bother the Waelz engineer nowadays as much as formerly it did.

The speed of rotation and the inclination of the kiln plays an important part in the control of its operation. The average rotation is one revolution in 55 sec. In some plants, to increase the throughput the speed of rotation was boosted up to one revolution in 30 or 40 sec. The charge, of course, moves forward at a greater speed and spreads itself in a thinner layer, causing a quick rise in temperature, due to the rapid increase in the rate of volatilization. This higher temperature leads to the formation of rings and for this reason the rotation was reduced back to the one revolution per minute. On the other hand, one plant reduced its speed to one revolution in 120 sec., which brought about a much greater depth of charge and slowing off of the volatilization, so that a great increase in the quantity of fuel was required to keep up the kiln temperature.

In designing a plant, due consideration must be given to the nature of the charge, for when the charge has a low melting point and can be easily slagged it is better to work with a low inclination, 2 per cent instead of 4 per cent. The charge does not move forward so fast and builds up a greater depth of charge. If with the lower slope the speed is increased to 40 sec. per revolution, practically ideal conditions have been created, in that depth of charge is caused by the low inclination and a greater turnover, mixing and change of surface by the increased speed, which tends to keep the temperatures within slagging limits yet at the same time gives the conditions required for volatilization.

It has already been stated that the object of the Waelz process is to drive off zinc, lead and other volatilizable metals and to concentrate them in a "fume." The composition of this fume varies with the materials being treated. A few examples are given in Table 1.

Generally speaking, the fume is not suitable for any other purpose than the recovery of the metals contained therein, though the oxide recovered from old muffle residues found a market with paint manufacturers for making up a light gray paint. Some firms manufacture a paint from the recovered oxide for use inside the works for protective purposes, where matched shades of color are not important. Paint made from these oxides has good covering power and is durable.

The behavior of silver is interesting. Under certain conditions, small amounts up to 20 per cent of the silver contained in the ore can be volatilized with the zinc and lead, but this silver cannot be revolatilized from the fume.

TABLE 1.—*Composition of Some Fumes*

From	Zinc	Lead	Tin	Copper
Lead smelter slags	66.5	6.5		
Old muffle residues	58.8	9.2		
Roasted blende	60.8	14.5		
Lead ashes	44.75	20.6		
Brass ashes and dross	63.93	11.56		
Zinc-copper ore	75.03		0.7	0.21

For transportation, the fume, a very fluffy, bulky material, must be sintered. From 1 to 10 per cent of coke is added to the fume and the mixed charge is passed through a smaller Waelz kiln. Here any lead present is revolatilized. The addition of a small quantity of common salt or ammonium chloride insures the complete elimination of the lead. Oxides carrying 15 per cent lead have been completely deleaded in this way. Further, this sintering drives off any chlorides and breaks up sulphites or sulphates in the oxide, and makes the sintered material suitable for treatment in the electrolytic zinc leaching plants.

The sintered fume consists of varying sized aggregates, from dust to large lumps, which are very hard and can be transported in bulk without any untoward losses due to dusting, etc. This material is suitable for any form of processing to recover the zinc.

The kiln residue, or clinker, becomes an important item when ores that contain nonvolatilizable metals of commercial value are treated, otherwise it simply goes to the dump, though use has been made of it as road material when worked up with tar or asphalt.

MANSFELD WORKS

The Mansfeld works has for several hundreds of years been one of the leading smelters in Germany for the production of copper and silver. The ore, a copper shale, carries less than 1 per cent of zinc and less than 0.5 per cent of lead. In 1924 soft lead was added to the list of metals produced and as an outcome of this in 1928 zinc oxide was being manufactured by means of the Waelz process. As it is the latter process that constitutes our main interest, we will confine ourselves to the stage of Mansfeld operations that led to the Waelz processing of the various slags and residues.

There are two smelters, Krug and Kock, both of which drive off zinc and lead in smelting the ore for the production of copper, mainly in the form of oxide but containing some sulphides. These oxides and sulphides are collected, by various standard methods, in the form of wet slimes having the average composition shown in Table 2.

TABLE 2.—*Average Composition of Oxides and Sulphides*

	Krug Smelter	Kock Smelter
Quantity per month (dry), short tons	660	1320
Lead, per cent	27	17
Zinc, per cent	21	26
Copper, per cent	0.8	0.8
Silver, per cent	0.2	0.08

To avoid slagging off the zinc in recovering the lead in a blast furnace, the Kock smelter treats its flue dust in a Waelz kiln to drive off *lead only*, leaving behind a zinc clinker. This is accomplished by adding to the flue dust some 10 to 15 per cent of coarsely ground raw lime and passing the mixture through a Waelz kiln heated with pulverized lignite. No other fuel is added. The lime helps to keep down the temperature and at the same time breaks up the charge. The greater part of the lead is fumed off as a sulphide, which in turn is roasted and oxidized in the hot gas current, being collected as an oxide by means of electrical precipitation. The analysis of the lead fume and zinc clinker recovered is given in Table 3.

TABLE 3.—*Analysis of Fume and Clinker at Kock Smelter*

	Lead Fume, Per Cent	Zinc Clinker, Per Cent
Lead	49.1	2.8
Zinc	8.7	34.4
Sulphur	9.6	9.6
Copper	0.35	1.6
Chlorine	3.00	
Cadmium	0.63	
Iron	0.85	2.3
Alumina	1.00	2.8
Lime	0.60	20.0
Silica	0.5	17.2
Silver	0.015	0.075

The lead fume is mixed with the flue dust from the Krug smelter and the mixture is sintered and treated in a lead-reduction furnace for the recovery of the lead and silver. The slag, which is granulated by water, has the following average composition: Zn, 20 per cent; SiO_2, 17; FeO, 36; Al_2O_3, 3; Pb, 1.5; Cu, 1.5; CaO, 5.0; S, 7.0. This slag, mixed with coke and the deleaded zinc clinker from the Kock smelter, is passed through a second Waelz kiln, where the zinc is recovered as an oxide having an average composition of Zn 71.5 per cent, Pb 5.6. The clinker, having an average composition of Zn 2.5 per cent, Ag 0.052, Cu 0.86, is returned to the copper smelter for inclusion in the smelting charge. The flowsheet for this procedure is given in Fig. 7.

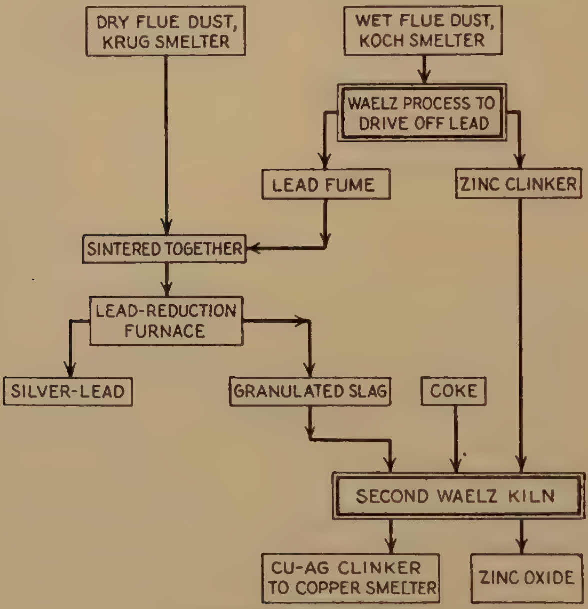


Fig. 7.—Flowsheet of the Mansfeld Works.

The lead smelter produces roughly some 19,800 short tons of slag per year; it has a slag dump formed of the accumulation of years, from which is worked an amount equal to that of the granulated slag, so that the charge going to the Waelz kiln carries about equal proportions of the two slags.

The Mansfeld Waelz plant consists of one small kiln some 66 ft. by 4 ft. effective diameter, and two larger kilns 100 ft. by 5¼ ft. effective diameter. These kilns are constructed of steel plate and lined with fire-brick and magnesite brick. They are supported on three bearings. Each kiln is motor-driven by direct gearing and a toothed rim, which is a part of the outer shell and is placed about halfway along its length. The kilns may be rotated by hand, to protect them from undue strains set up by the hot stationary charge.

Direct current is used on the kilns and fans to allow for speed control. The rotation of the kiln can be varied from one revolution in 36 sec. to one revolution in 70 sec. but the running average is one revolution in 55 seconds.

The charge to the second Waelz kiln consists of zinc clinker from the first kiln, granulated slag from the lead smelter, and coke, plus an equal amount of slag from dump, which is not shown on the flowsheet. These materials are carefully weighed, mixed and fed to the kiln by Marcus conveyors through water-cooled chutes. These chutes use some 875 gal. of water per hour for cooling purposes, and to facilitate the movement of the charge they receive some 90 impulses per minute by means of a mechanical tapper. All mechanical operations other than the kilns and fans are operated on alternating current. Actually, the Waelz plant, including all incidental machines, consumes some 18 kw-hr. of three-phase alternating current and 12 kw-hr. of direct current per ton of slag treated.

It is worth noting that the charge contains a fusible slag with a melting point below 1100° C. It has been the custom to add lime as a stiffener for the charge, but it was found that an excess of coke permitted elimination of the lime and an increase in throughput. The quantity of coke used in making up the charge varies according to the quality, from 25 to 28 per cent.

The kilns have a capacity of 55 tons of slag per 24 hr. In operation the kilns are first fired by means of powdered coal or oil until the required temperature for the reducing reactions is reached, after which the heat of these reactions is sufficient to maintain the required operating temperature, so that only occasional heat from auxiliary source is necessary. Actually the cost of this auxiliary firing is below 6¢ per ton.

CONCENTRATION

Table 4 shows the results of selective flotation of a complex zinc-copper ore.

TABLE 4.—*Results of Flotation of Complex Zinc-copper Ore*

Ore	Copper Concentrate, Per Cent		Zinc Concentrate, Per Cent	
	Metal	Recovery	Metal	Recovery
Quantity, 100		9.9		
Copper, 2.50 per cent	23.4	93.9	0.48	5.0
Zinc, 15.30 per cent	9.25	5.9	55.25	91.7
Gold, oz. per ton, 0.025	0.14	54.4	0.02	20.3
Silver, oz. per ton, 3.42	33.46	71.3	2.98	16.6

In marketing these concentrates the usual schedules show payment for the copper and precious metals in the copper concentrate, but demand a penalty of 25¢ per unit for all zinc over 5 per cent. There are other penalties as well, which greatly reduce the value of the concentrate. In the zinc concentrate only the zinc is paid for, so that the mine eventually is paid for 93.9 per cent of the copper, 91.7 per cent of the zinc, 54.4 per cent of the gold and 71.3 per cent of the silver in the ore, less the smelter deductions and penalties, so that the loss in precious metals alone constitutes a serious problem.

TABLE 5.—*Mixed Concentrates*

Ore	Recovery, Per Cent
Quantity, 100	35.8
Copper, per cent, 6.8	98.9
Zinc, per cent, 39.8	97.6
Gold, oz. per ton, 0.053	74.6
Silver, oz. per ton, 11.5	87.9

If the two concentrates are mixed together the percentage of metals available for payment is considerably increased (Table 5) but only the Waelz process could economically treat such a mixed concentrate. If, then, in an effort to save the precious metals, it is decided to mix the concentrates, it would be better to just drop the gangue and beneficiate the ore; in other words, make a "bulk float" (Table 6). These figures show a greatly increased recovery of precious metals. The important consideration here is to strike such a balance as to give a copper content to the concentrate that will make the recovery of this copper from the Waelz clinker worth while, and at the same time keep the zinc down to workable limits, for it must be pointed out that the Waelz process was primarily designed to treat low-grade material. The process therefore demonstrates its elastic applicability when it can treat a 30 per cent zinc concentrate with results as good as when it treats the simpler low-grade material.

TABLE 6.—*Bulk Float*

Concentrates	Recovery, Per Cent	
Quantity, 100		45.3
Copper, per cent, 2.92	6.28	97.5
Zinc, per cent, 13.45	27.50	98.7
Gold, oz. per ton, 0.025	0.06	83.5
Silver, oz. per ton, 4.35	10.50	94.4

Fig. 8 is a flowsheet for the treatment of a complex zinc-copper ore.

In the treatment of the bulk concentrate given in Table 6 the analysis of the roasted material ran: Cu, 8.00 per cent; Zn, 37.45; Pb, 0.78; Fe, 24.25; S, 4.60; insol., 2.50; Ag, 14.00 oz. per ton; Au, 0.116 oz. per ton. This was mixed with the usual amount of coke, about 24 per cent of the charge, and passed through the Waelz kiln, and 97.5 per cent of the zinc was recovered as an oxide running 73.05 per cent zinc. The clinker, with a composition of 13 per cent Cu, 20.8 oz. Ag, and 0.169 oz. Au, shows a recovery of 97.5 per cent of the copper and gold, with 96 per cent of the silver.

OTHER ORES

In a large plant in Germany lead is volatilized as a sulphide from a lead ore having a high silica content. The run-of-mine ore, which contains between 1 to 5 per cent Pb, is concentrated by wet concentration and gives a middling product assaying 12 to 15 per cent Pb. These jig middlings are then treated by the Waelz process and the resulting lead fume (99 per cent recovery) is added to the charge of the usual smelting operations.

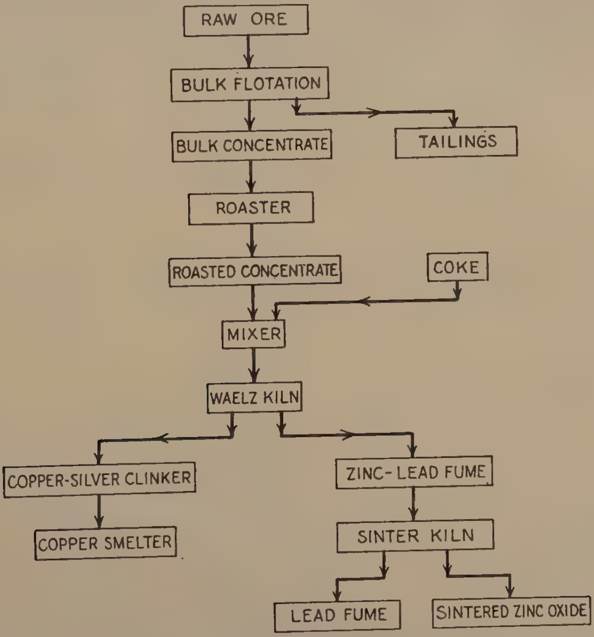


FIG. 8.—FLOWSHEET FOR TREATMENT OF COMPLEX ZINC-COPPER ORE.

A plant at Sturzelburg, Germany (Fig. 9) treats purple iron ore, volatilizing off the zinc and leaving an iron clinker for smelting.

The recovery of tin is another interesting application of the Waelz process. Tin can be volatilized as a sulphide with a high degree of efficiency. The tin ore is mixed with pyrite, gypsum or other sulphur-bearing materials and fed to a Waelz kiln. During the reaction in the kiln the tin oxide is converted into tin sulphide and in this form is easily fumed off. This tin sulphide is reconverted into oxide by the hot flue gases and is precipitated out from them in that form. The residue discharged from the kiln averages, as a rule, 0.1 to 0.2 per cent Sn, which corresponds, according to the content of the ore, to a 95 to 99 per cent recovery. This method of recovery of tin is in operation on a large scale in Germany.

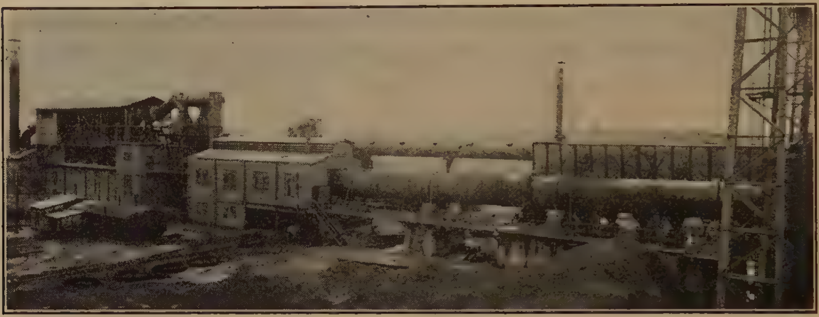


FIG. 9.—WAELZ PLANT AT STURZELBURG FOR TREATING PURPLE IRON ORE.

Very low-grade tin ores, by a combination of concentration and the Waelz process, have been made to yield up to 99 per cent of the tin as tin oxide. Any arsenic, antimony, lead, or sulphur can be eliminated from the recovered tin oxide by subjecting it to a sintering treatment through a secondary kiln.

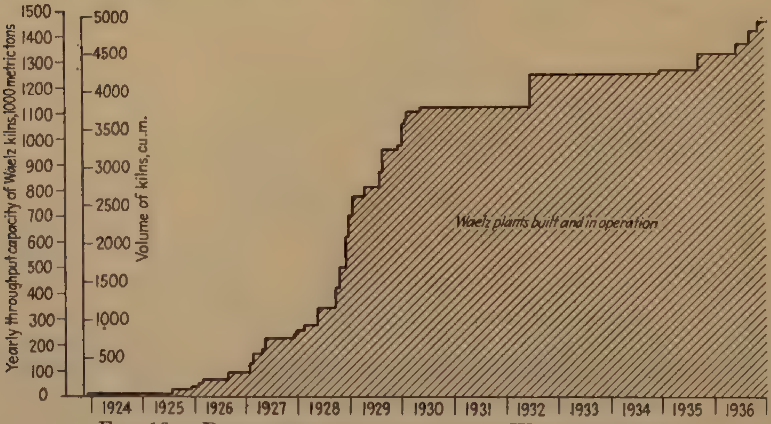


FIG. 10.—DEVELOPMENT IN USE OF THE WAELZ PROCESS.

In the treatment of arsenic-antimony gold-bearing ores or concentrates, the Waelz process offers a simple yet efficient method of separation. In one plant flotation concentrates were obtained having the following composition: Sb, 20 to 40 per cent; As, 8 to 13 per cent; S, 18 to 23 per cent and Au, 6 to 6½ oz. per ton. Cyaniding was out of the question; experimental work on ordinary roasting did not bring about the desired results; but by means of the Waelz process a clinker is produced that contained only 2 per cent of arsenic-antimony combined with the gold concentrated to 15 to 16 oz. per ton. This clinker is mixed with old lead and litharge and smelted in a shaft furnace, the recovered gold-bearing lead being treated and refined on a cupeling hearth and giving a gold recovery averaging 98 per cent. As the litharge produced is passed back to the furnace operations, the loss in lead is exceedingly small, making the whole operation economical and efficient.

TABLE 7.—*Waelz Kilns in Operation*

Location	Number of Kilns	Size	Year Built	Material Treated
Luenen, Germany	1	130′0″ by 6′6″	1925	Brass ashes, zinc ores.
Lipiny, Poland	1	78′0″ by 6′0″	1925	Blende slimes.
Beuthen, Germany	1	98′0″ by 6′0″	1926	Calamine tailings.
	1	130′0″ by 7′0″	1927	
Brzeziny, Poland	5	130′0″ by 10′9″	1928	Calamine ores and tailings.
	1	98′0″ by 6′6″	1926	Sintering oxide.
Mansfeld, Germany	1	66′0″ by 5′4″	1925	Sintering.
	2	98′0″ by 6′6″	1927–28	Zinc-lead fume and slags.
Mechernich, Germany	1	130′0″ by 6′6″	1927	Jig middlings.
	1	130′0″ by 9′0″	1929	Jig middlings.
	1	130′0″ by 9′0″	1936	Jig middlings.
Beuthen, Germany	2	130′0″ by 7′4″	1927	Blende, calamine slimes.
	1	42′6″ by 4′3″	1927	Sintering.
Brzosowice, Poland	1	130′0″ by 6′6″	1927	Calamine slimes.
	1	130′0″ by 10′0″	1935	Calamine slimes.
	1	42′6″ by 4′3″	1929	Sintering.
Thasos, Greece	5	42′6″ by 4′0″	1927	Calamine tailings.
Denora, Pa., U. S. A.	1	137′9″ by 10′0″	1928	Muffle residues.
Sturzelburg, Germany	1	130′0″ by 7′6″	1928	Zinc-bearing purple ores.
La Calamine, Belgium	1	130′0″ by 7′4″	1929	Calamine slimes.
Duisburg, Germany	1	65′6″ by 4′6″	1929	Tin ores and slags.
Palmerton, Pa., U. S. A.	1	138′0″ by 10′0″	1929	Zinc ores, residues.
	1	160′0″ by 11′3″	1930	Zinc ores, residues.
Iglesias, Sardinia, Italy	1	137′9″ by 11′0″	1930	Middlings, concentrates.
	1	65′0″ by 7′0″	1930	Sintering.
Tindale, England	1	98′0″ by 7′6″	1930	Muffle residues.
Fukushisuaken, Japan	1	98′0″ by 6′6″	1930	Electrolytic zinc leach residues.
La Salle, Ill., U. S. A.	1	125′0″ by 10′0″	1932	Muffle residues.
Nordenham, Germany	1	72′0″ by 6′0″	1934	Muffle residues.
Danville, Ill., U. S. A.	1	125′0″ by 8′0″	1936	Muffle residues.
Cherryvale, Kans., U. S. A.	1		1936	Residues

PLANTS IN OPERATION

In the course of 12 or 15 years, eight plants have been built in Germany, three in Poland, five in the United States of America, and one each in England, Italy, Japan, Greece and Belgium; altogether 41 kilns having a total capacity of about one and one-half million tons and producing over 200,000 tons of zinc oxide and 25,000 tons of lead oxide per annum. Fig. 10 shows graphically the development of the use of the process and Table 7 lists the Waelz kilns that have been built with their sizes, location and material being treated.

Slag Treatment for the Recovery of Lead and Zinc at Trail, British Columbia

By R. R. McNaughton*

The Consolidated Mining and Smelting Company of Canada, Ltd. at Trail, B. C., inaugurated a comprehensive program of investigation about 15 years ago to develop the most economical process of recovering the metal in the large accumulated stock of by-products of the lead smelter and the zinc plant. Two principal methods of recovery were followed to a successful conclusion—an electrothermic process to treat zinc-plant residues and cold slag and the fuming of hot slag from the lead blast furnaces. The latter was selected because it showed a saving over the former in its ability to handle hot blast-furnace slag, thus obviating the necessity of granulating, handling and eventually remelting the same slag for the electrothermic process.

The design of a fuming plant was commenced in 1928, and construction, which was started immediately, was completed in July 1930. Operating intermittently for a general tuning up, the plant was officially blown in for regular operation in August. During this month the vagaries of a slag-fuming plant were studied and an operating crew was trained. A history of slag fuming at Trail and the development of plant design is given in a paper by G. E. Murray in the *Transactions* of the Canadian Institute of Mining and Metallurgy for 1933.

FUMING PLANT

The fuming plant at Trail (Fig. 1) is a separate unit although of necessity interlocked closely with the lead smelter. The plant consists essentially of a fuming furnace with its accessories, a waste-heat boiler followed by an economizer, and a suction-type baghouse. The plant was built as the first of two 400-ton units with the intention of adding the second unit within a year, so that flues, fans and buildings were built to handle double the original load.

Furnace.—The furnace as originally built (Fig. 2) was of water-jacket construction, 10 ft. wide, 20 ft. long and 6 to 10 ft. high. The roof height was made variable to check experimental work, which had indicated that this dimension affected the rate of reduction. Coal and air were supplied

---

Manuscript received at the office of the Institute July 20, 1936.

* Assistant Smelter Superintendent, Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C.

through 35 double-inlet tuyeres on each side of the furnace. These tuyeres are the invention of Alexander Laist, of Anaconda. Coal feeders, five for each side of the furnace, were of screw type, $3\frac{15}{16}$-in. dia. by $1\frac{1}{2}$-in. pitch, each driven through its individual variable-speed transmission by a 1-hp. motor. Air at 4 to 8 lb. pressure was supplied by a turboblower, which was a legacy from copper-converter operations. Fitted with a constant-volume regulator, the blower supplied 15,000 cu. ft. per min. between the pressures noted. Lead-furnace slag was charged from 9-ton pots by the crane that served the blast furnaces and re-treated slag was tapped through two $5\frac{1}{2}$-in. tapholes to a granulating launder.

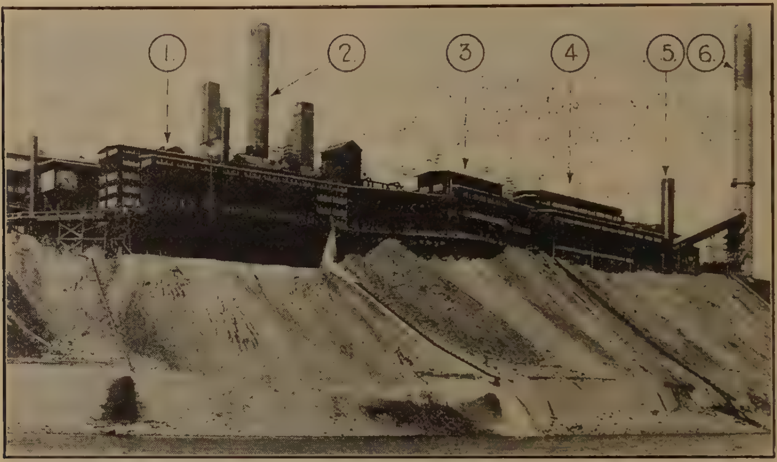


FIG. 1.—SLAG-FUMING PLANT, CONSOLIDATED MINING AND SMELTING COMPANY OF CANADA, LTD., TRAIL, B. C.

1. Furnace and boiler building.	4. Baghouse.
2. Lead-furnace stack.	5. Baghouse stack.
3. Economizer.	6. Dwight-Lloyd stack.

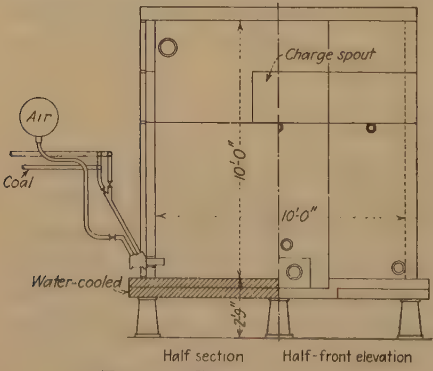


FIG. 2.—SLAG FURNACE.

Gases loaded with lead and zinc oxides left the furnace through a throat of variable area in the roof to rise 21 ft. to a short horizontal flue. Up to this point the flues were entirely water-cooled.

Boiler.—Two B. & W. Stirling boilers, each of 17,350 sq. ft. heating surface, were connected by a brick flue in such a manner that furnace gases could be directed through either. The distributing flue and boiler inlet flues were liberally hoppered to facilitate cleaning. Boilers were equipped with 32 steam soot-blower elements, which, it was anticipated, would be of considerable assistance in keeping tube surfaces clean. No ordinary gas-cooling problem was being undertaken: the total load of dust entering the boiler was 87 tons per day and, to make matters worse, the load varied periodically from a minimum rate of 2¼ tons per hour to a maximum of 17¾ tons. To aggravate the situation further, the dust was fusible at the temperatures prevailing at the boiler inlet, and provision had to be made to allow for hand-lancing. A condenser was installed capable of handling 110,000 lb. per hour, double the production from one boiler, in case the demand for steam did not increase above that evident at the time. Water-softener and treatment plants were included, of course.

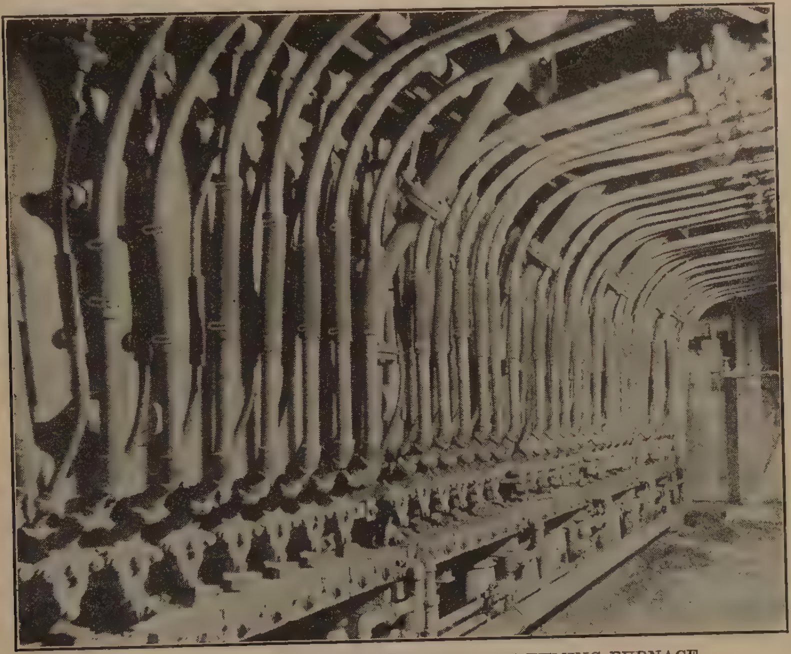


FIG. 3.—PRESENT CONSTRUCTION OF SLAG-FUMING FURNACE.

Twenty-five hundred pounds of gas entered the boiler per minute at 2200° F., generated 53,600 lb. per hour of 185-lb. steam at 500° F. and reached the breeching at 630° F. Boiler draft was supplied by a paddle-wheel fan having a capacity of 233,000 cu. ft. per min. of 700° F. gas at 4 in. of water. Boiler draft loss amounted to 0.7 in. of water, so that 1.0-in. draft at the boiler outlet gave 0.3 in. at the furnace throat. This fan, which will be referred to as fan A, was driven by a variable-speed motor through Texropes and delivered the gas through a 238-sq. ft. hoppered steel flue to the economizer inlet at neutral draft.

Economizer.—The Green economizer consisted of 1008 cast-iron tubes, 4 in. inside diameter and 12 ft. long, arranged in 84 banks 12 tubes wide.

Scrapers were of the "crab-jaw" type, which clean on the upward travel only. In order to ensure maximum clearance for dust, the bottom headers were of special ovoid section. Tubes were spaced at 8-in. centers across the bank, with 7¼ in. between bank centers.

Some heated water was circulated back to the feed water to keep the tube temperature above the dew point of the gas, and hot water in excess of boiler-feed requirements was wasted.

Gases entered the unit at a little under 600° F. and were drawn off at 250° F. by the fan B. A damper panel in the flue roof allowed further cooling by leakage air when necessary. Dust that dropped in the flue system preceding this fan was loaded from the flue hoppers into narrow-gauge 58-cu. ft. V-cars and trammed to the oxide leaching plant.

Baghouse.—The B fan, able to handle 300,000 cu. ft. per min. of 230° F. gas at 2 in. of water, had also a variable-speed Texrope drive and delivered the gases to the baghouse inlet flue at neutral draft. The Dracco baghouse had six 10-compartment units of 18 woolen bags each, and sufficient floor space was available to increase the capacity by 50 per cent. Baghouse fume dropped into 9-in. closed screw conveyors under each row of five compartments, was delivered to two 12-in. collecting conveyors and eventually discharged onto an 18-in. belt. This belt ran 363 ft. to a bin mounted 68 ft. above and to one side of standard-gauge tracks. Special closed 2620-cu. ft. cars carried the fume to the oxide leaching plant for further treatment.

The final fan in the system, known as fan C-1, had a capacity of 150,000 cu. ft. per min. handling 200° F. gas at 4½-in. draft. A duplicate fan, C-2, was installed at the same time and connected to the outlet flue for the second baghouse unit, which had been temporarily arranged to by-pass the baghouse. Both C fans discharged into a stack 14 ft. 6 in. in diameter and 100 ft. high.

Operating Difficulties

One of the first difficulties that was encountered in operation of the plant was that of controlling the rate of coal feed within reasonable limits. The problem of feeding the fuel is in itself unusual in that the coal is discharged from the tuyere pipes against a 7-lb. or 8-lb. back pressure. However, owing to the success of experimental work, no trouble was anticipated in feeding coal, and there was none. The trouble was to control the rate at which the coal was fed. The solution of this problem lay in correlating the rate of waste-heat steam generation with coal feed.

A flowmeter was installed at the furnace floor for the benefit of the coal-feeder operators, who adjust the speed of the feed screws to maintain the steam flow at a constant rate. It has been found by experience that the coal feed corresponding to this rate of steam generation will give the maximum rate of zinc elimination from the charge. Feeding faster than at this optimum rate does not result in faster elimination, and feeding at a slower rate will slow down the elimination rate.

A further and rather more serious difficulty was encountered in the rapidity with which the hot flues filled with slag. Lead and zinc oxides with coal ash and slag bubbles carried by the furnace gases stuck to the brick walls of these flues and there acted as an excellent flux to slag off the brick. The resultant slag was very fusible and ran down the walls and into the flue hoppers where, being relatively cooler, it became a viscous mass, which resisted all efforts to remove it. The solution of this problem was rather obvious and will be discussed in detail later.

The amount of pot shell produced in collecting blast-furnace slag came somewhat as a surprise; 42 per cent of the new slag-forming material in the blast-furnace charge made shell and was charged back to the blast furnaces for reasons that will be set forth below.

These three difficulties were not the only ones, of course, that occurred during the early months of operation, but they were the most troublesome.

PLANT ALTERATIONS

Modifications have been made in the original design of the plant to meet economic or operating needs. These changes will be dealt with not in chronological order but under unit headings starting with the collection of blast-furnace slag.

Holding Furnaces

In order to reduce the excessive production of pot shell, two 40-ton holding furnaces were built. Each furnace collects the slag from two blast furnaces, keeping it hot between fuming-furnace charges. These furnaces have hearths 10 ft. 6 in. by 18 ft., and are built of firebrick above the slag line with the lower walls water-jacketed. They use 6 tons of powdered coal per furnace day. The furnace gases are drawn off through a vertical brick-lined steel stack connected to the blast-furnace balloon flue. Shell production amounts to 15 to 20 per cent, depending on the condition of the blast-furnace slag. A reducing atmosphere is maintained to reduce spinels, and silica sand is spread over the hearth after each tap, to flux the ferrous compounds.

Slag is tapped through a 12-in. notch into a pot set into the tapping pit in the crane aisle. A swinging hood exhausts the smoke caused by tapping, through a No. 3½ Sirocco fan to a stack discharging above the roof of the feed floor.

Fuming Furnace

Before the plant had been in operation a year several furnace jackets had failed in an unusual manner. The furnace walls had been built with three tiers of jackets, so that the height of the roof could be varied, as explained previously. These failures occurred only in the lower tier of jackets in the form of a vertical crack close to the middle and in the lower third of the jacket face. The cracks appear to be the result of fatigue but investigation has not identified the exact manner in which this takes place. Stiffening the jacket face with a flat bar grid welded to the front and back plates (Fig. 4) has at least reduced the trouble.

Tests seem to show that ½-in. plate of "firebox" quality has less tendency to crack than plate of higher tensile strength. Stress relief by annealing after welding has no effect on jacket life. Test jackets of copper plate or of high-temperature steel show no advantage in length of service commensurate with their cost.

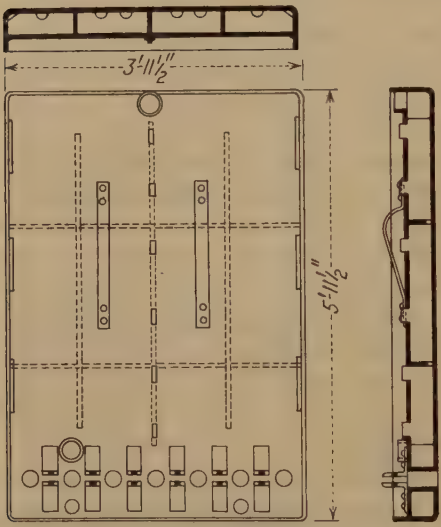


Fig. 4.—Original construction of slag-fuming furnace and flues.

The Nesmith vaporizer system of jacket-water control finds an ideal application in the fuming furnace. Heat release to the jacket water depends on the thickness of the coating of slag on the individual jacket faces, which may vary instantaneously from several inches to nothing. Instead of having constantly to adjust the feed water on jackets, the furnaceman now can forget that there is water in the jackets. Incidentally, the saving in cooling water is considerable. The vaporizer system was installed at the same time that the furnace length was extended to 24 ft. in 1931.

It had been fairly well established that furnace capacity was a function of the length, so that an increase of 20 per cent in furnace length indicated a corresponding increase in production, which was obtained.

Variation in the roof height showed no effect on rate of elimination in practice, and the roof was finally set at 10 ft., as this dimension was most satisfactory for structural reasons. A furnace with a high roof—in other words, with a larger volume above the charge—will have less tendency to smoke than one with a low roof, owing to its ability to absorb the sudden puffs of gas produced by the miniature explosions taking place in the furnace. The furnace as it exists today is shown in Fig. 5.

Coal Feeders

In order to reduce high maintenance costs, the original arrangement of individual feeder drives was changed so that each group of five feeders

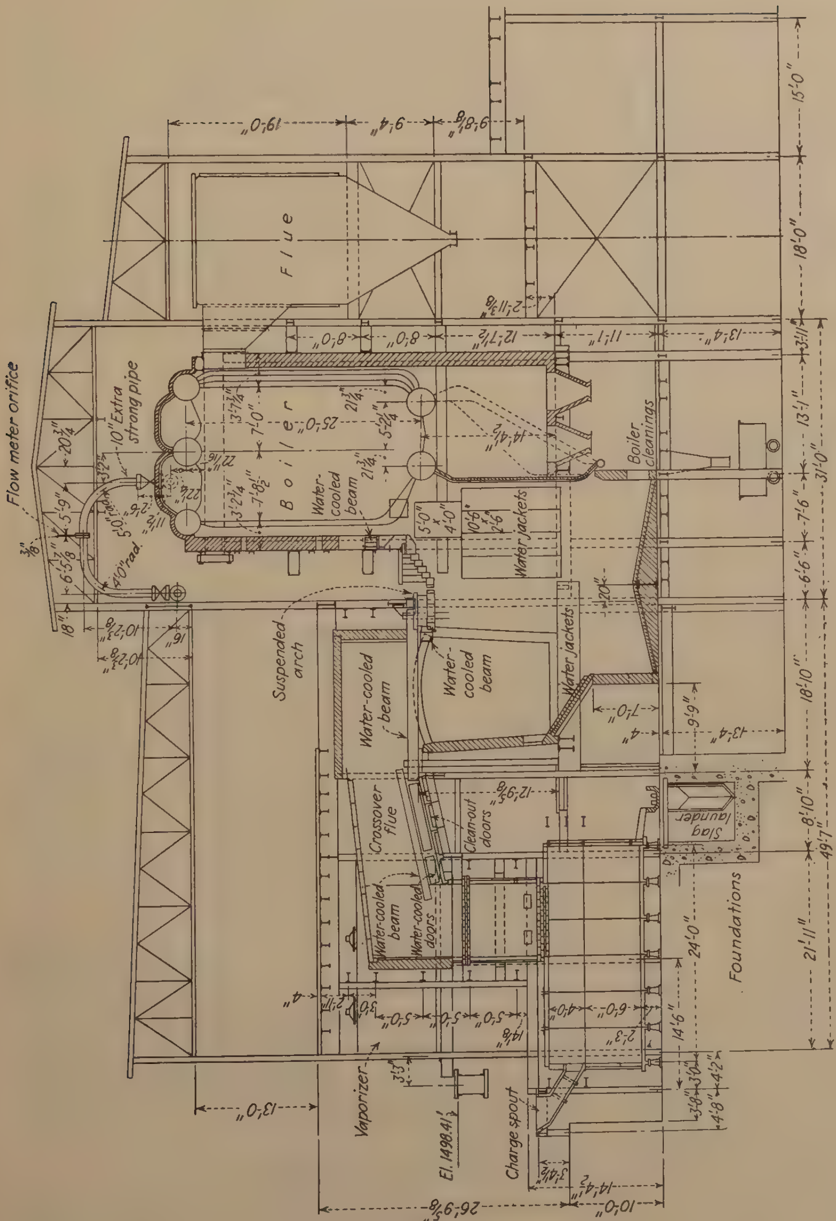


FIG. 5.—PRESENT CONSTRUCTION OF SLAG-FUMING FURNACE AND No. 1 BOILER.

would be driven by a single motor through a locally designed variable-speed transmission. An auxiliary motor drives the screws at normal speed and dog clutches allow any feeder or group of feeders to be stopped for tank filling or repairs. Screws turn at a normal 250 r.p.m., and the severe wear on clutch points is minimized by Stelliting the points.

Coal-transport pipes have been increased from 2 in. to 2½, with a notable reduction in line plugging and a decrease in the volume of high-pressure air used at the injectors. The original arrangement of transport pipes, which allowed the center coal feeder to feed any or all of the four 2½-in. lines supplying the tuyere headers, has been entirely satisfactory.

Launder

The launder troughs, until now of white cast iron, will shortly be replaced by ½-in. rubber, which is cheaper, lasts longer and is more easily repaired.

Brick Flues

The short flue connecting furnace uptake and distributing flue, known locally as the "crossover," was built entirely of water jackets with a level floor (Fig. 6). Owing to the increasing demand for steam, roof and side-wall jackets were replaced by brick, which resulted in the generation of an additional 200,000 lb. of steam per day. The section of the roof over the furnace uptake had a life of only four months and introduced a fire hazard, as this roof was immediately under the lead-furnace feed floor. To avoid the necessity of frequent replacements, this part of the roof was later replaced by water jackets. To assist cleaning, the water-jacketed floor of this flue was sloped down towards the furnace uptake (Fig. 5).

Since it was impossible to remove the slag from the hoppers in the floor of the inlet flue (Fig. 6), these were cut out to make slag pockets that extended down to the furnace floor. These pockets have been progressively enlarged until, as shown in Fig. 5, the entire floor of the boiler inlet flue has been dropped 11 ft. This construction became possible only when it was demonstrated that the continuity of boiler operation was equal to that of the furnace and inlet dampers could therefore be discarded.

One consequence of enlarging this flue was that the slag, in its progress down the walls, solidified and stuck to the walls as it left the hot upper zone of the flue. In the course of a few months, scabs would build out from the walls until they met and arched across the 20-ft. space, necessitating a shutdown for digging, or rather, mining. In order to cope with this situation a water wall was installed in place of the brick bridge wall below the front mud drum, and water jackets, at the sacrifice of some waste-heat steam, were set into the side walls at strategic points.

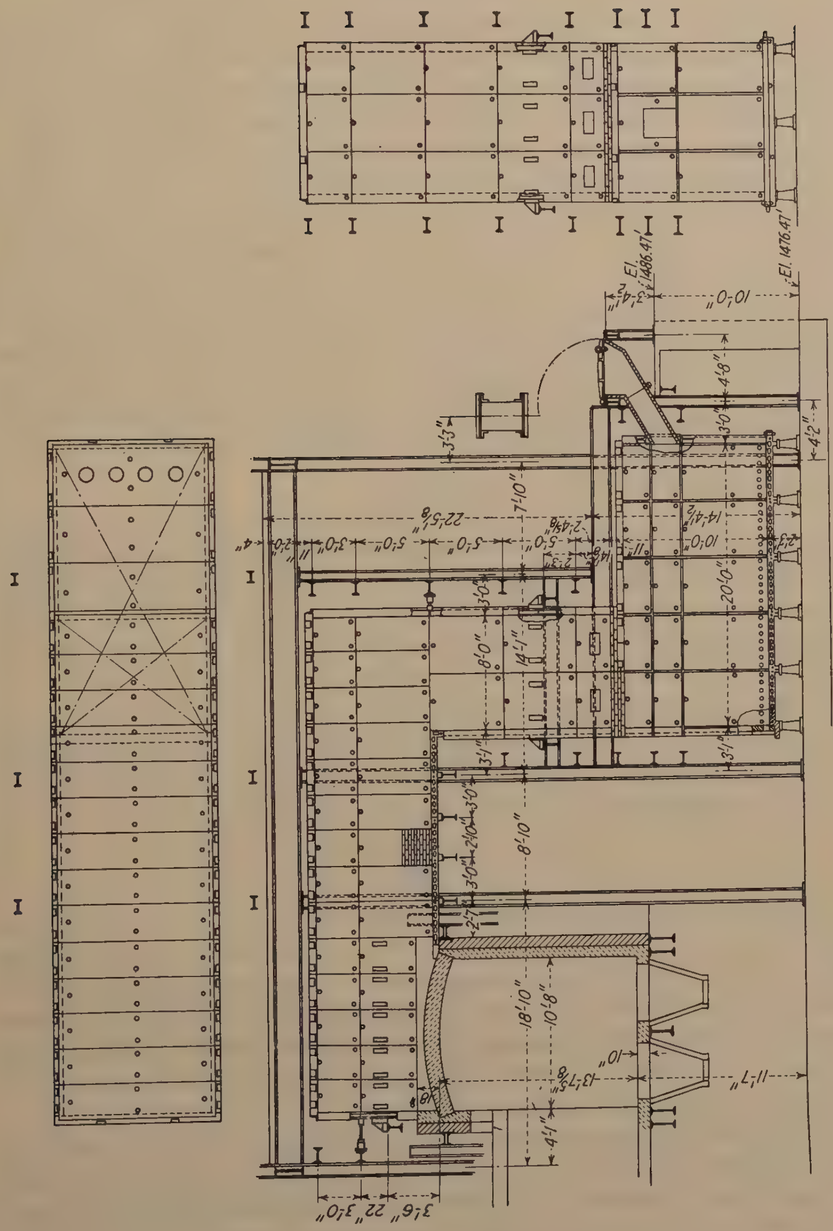


FIG. 6.—ORIGINAL CONSTRUCTION OF SLAG-FUMING FURNACE AND FLUES.

As slag will not build on either the water wall or jackets, this construction has been entirely satisfactory. When it became necessary to increase the auxiliary steaming capacity, which must be available when the fuming plant is shut down, the auxiliary boiler, which occasionally handled waste-heat gases, was remodeled with water-walled inlet flues[1].

The rapidity of brickwork corrosion in the hot flues has been a motive for the investigation, still in progress, of many different refractories in this service. To date it has been shown that cheap firebrick laid up in as thin a wall as the height allows is more economical than any higher priced brick regardless of composition. Walls are given a slight batter to lean outwards so that when the brick becomes thin the tendency is for the wall to fall away from the flue against supporting steel outside. Relieving arches have been replaced by water-cooled structural steel beams and hot sprung arches have been replaced by suspended flat roofs (Fig. 3).

Dampers

Hot-flue drop dampers, originally used in directing the waste-heat gases to either boiler, were 9 ft. 3 in. wide by 11 ft. 5 in. high with a 2-in. water space between ½-in. plates stayed at 12-in. centers. Handled by 5-ton chain blocks, their manipulation was awkward, although it was at least assured that water circulation would be established before the entire damper surface was exposed to the heat.

Louver boiler-breeching dampers were replaced by plate drop dampers. In fact, louver dampers are unsuitable for service in any part of the flue system unless they are in more or less constant use.

Boiler

The boiler has given remarkably little trouble and the few difficulties have been overcome easily. There were a number of failures in the first bank of tubes, due to sluggish circulation. The space between the upper vertical run of this bank and the front wall had been reduced by movement of the wall and the accumulation of clinker until the passage was blocked. Removal of this row of tubes has remedied the trouble with no increase in breeching-gas temperature.

Steam soot blowers, although very desirable, have been discontinued in the first pass because zinc oxide attacks them at the prevailing temperature and their life is very short. High-temperature-resisting steel as well as nickel-chrome alloys have been tested in this service, but the cost is prohibitive for the slight increase in life.

Heat-resisting steel baffles in each pass warped badly and have been replaced by tile.

---

[1] W. H. D. Clark: *Can. Min. Jnl.* (Sept., 1932).

It has been difficult to maintain a tight boiler setting owing to the large number of doors necessary for constant hand-lancing, so that air leakage amounts to a normal 100 per cent across the boiler.

Flues from the boiler outlet to the baghouse remain as they were originally constructed. Hoppers were let into the outlets of the A and B fans in order to prevent accumulated dust from sliding back into the fan and endangering the runner.

Economizer

Trouble in the operation of the economizer had to do particularly with cleaning. A row of 3 by 4-in. doors was placed in the casing opposite the spaces between bottom headers, when the unit was built. These were suitable for hand-lancing to ensure a clear passage for falling dust but had to be augmented by a row of 6 by 14-in. doors 2 ft. higher and another 2 ft. below the upper headers. These additional doors assist in freeing stuck scrapers and in general cleaning.

The service required of this unit is considerably more severe than it would be in handling boiler gases and it is gratifying that the operation has been so satisfactory.

Baghouse

In the first few months of operation the volume of gas cleared by the baghouse gradually dropped. Investigation showed that fume was building up on the nap fibers of the woolen bags in small nodules, which effectively blocked the passage of the gas. The bag weight was also increasing, so that the shaking mechanism acted sluggishly. The baghouse was enlarged, to increase filtering area by one-third, and it has been necessary to wash the bags every three or four months in order to maintain filtering capacity.

Owing to the necessary frequency and severity of rapping, the wear on bag racks and hangers has been excessive and some modification in their design has proved advantageous. Bag hangers have been case-hardened and hanger holes in the racks have been bushed.

When it developed that the life of woolen bags would be somewhat less than 12 months, an investigation of other and cheaper bag materials was started. Neither cotton nor linen will stand the temperature, and it appears that the most economical bag is one made of llama wool. A laundry and tailor shop have been added as baghouse accessories.

OPERATION

Lead-furnace slag is tapped from the holding furnaces and transferred as quickly as possible by 20-ton lead crane to the fuming furnace on the opposite side and at one end of the crane aisle. It takes about 20 minutes to charge 10 pots of slag; that is, 65 to 70 tons. Pots are shelled on a heavy, structural-steel grizzly over a 100-ton bin at one end of the craneway and the broken shell is returned to the blast furnaces.

The fuming furnace operates on a 155-min. cycle. Allowing 20 min. for charging and 10 min. for tapping leaves 125 min. for blowing the full charge. The coal feed remains constant throughout at approximately 6 tons per hour.

Coal, crushed in a central preparation plant to 85 per cent through 200 mesh, is delivered by the Quigley system to two 40-ton cylindrical steel bins, one on each side of the furnace. An average speed of 250 r.p.m. on eight or nine screw feeders maintains waste-heat steam flow at the optimum 60,000 lb. per hour, which corresponds to the maximum elimination rate. The feeders, mounted on the hopper bottom of individual pressure tanks, drop the coal into 80 lb. per sq. in. air injectors, which project it into 2½-in. transport pipes. A header on the end of each transport line supplies eight or nine tuyeres through ¾-in. pipes. Coal from the center feeder can be split into any of the four supply lines on each side of the furnace.

Air is supplied at a constant volume of 15,000 cu. ft. per min. at a pressure of from 4 to 8 lb. per sq. in.; 80 lb. per sq. in. injector air amounts to 34 cu. ft. per min. per feeder.

Slag is tapped below the tuyere level through two 5½-in. tapholes set in a water-cooled cast-iron block. Passing through a rectangular receiver, the slag is split into three streams, each of which is struck by a 2½-in. jet of water at a pressure of 70 lb. per sq. in. Low-pressure zinc-plant waste water sluices the slag down the launder. Granulation water amounts to 2.6 tons per ton of slag.

The constitution of the furnace charge depends on the quantity of hot slag available. Roughly, 2½ tons of granulated lead-furnace slag blown in above the charge will replace 6½ tons of hot slag with the same resulting elimination rate. An estimate based on 85 per cent zinc elimination in a normal cycle determines the amount of granulated slag that should be added to a charge deficient in hot slag. The furnace will treat 600 tons of hot slag in 24 hr., under normal conditions, with a recovery of 85 per cent of the zinc and 98 per cent of the lead.

Constant vigilance and a regular routine of cleaning flues and boilers are necessary to maintain furnace draft at a maximum. The crossover flue is cleaned by blowing with a hand lance. Cleanings either fall back into the furnace or are pushed ahead into the inlet flue.

Cleanings from the first pass of the boiler drop into the inlet flue also and are raked out over a grizzly, which separates coarse chunks of slag or "clinker" from fine semifused oxide "cleanings." The fines are delivered to the zinc plant for crushing and leaching, while the clinker is crushed and re-teaed rtin the fuming furnace.

Dust from the last two boiler passes and from the rest of the flue system as far as the baghouse inlet, is collected by contract labor and trammed in 58-cu. ft. V-cars on narrow-gauge track to the oxide leaching plant.

Draft gauges at the boiler inlet and breeching flues indicate draft loss and a recording thermometer shows the temperature of outlet gases. Thoroughness of boiler cleaning is indicated by draft loss, outlet gas temperature and steam temperature.

As mentioned previously, the use of steam soot blowers is confined to the second and last passes, while all tube surfaces in the first and second passes must be accessible to the hand lance. A long-distance water gauge is located on each side of the boiler at the level of the mud drum, for the convenience of the boiler operator.

The baghouse attendant is responsible for the operation of the plant from the boiler outlet to the stack. He blows down A and B fan outlet and inlet flues once a shift, to avoid slides. The economizer must be lanced every charge to make sure dust clears into the hoppers below. The water temperature, indicated on a recording thermometer chart, requires frequent adjustment to keep the feed water at 80°F. Another recording thermometer with a maximum alarm set at 210°F. indicates the temperature of the gas at the baghouse inlet. The operator adjusts the air-inlet dampers to control the temperature at this point.

Each section of the baghouse is inspected once in 24 hr. for dust leaks, and a notation is made on a report card for the attention of the baghouse repair crew. Consisting of two men, this crew, working on the day shift only, keeps the dust loss at a minimum and changes the bags in suitable rotation so that the maximum gas volume is handled at all times.

On removal from service, bags are soaked in cold water for two weeks, then agitated by air in a tank of water, where most of the dust is washed out. Hand-scrubbing finishes the washing and the bags are dried before going to the tailor shop for inspection and repair. After three periods of service, the bag material is usually too weak for further use, and such bags are scrapped.

The operating crew consists of:

1 foreman
3 furnacemen
3 furnace helpers
6 coal operators
3 boiler operators
3 boiler helpers
3 baghouse operators
6 dust men
1 baghouse car loader working six days per week
2½ pot-shell loaders

The baghouse repair crew works 5½ days per week, and includes:

1 repairman
1 repairman helper
1 tailor
1 bag washer

METALLURGY

The reactions involved in the fuming operation may be indicated by three end equations:

$$2C + O_2 \rightarrow 2CO \qquad [1]$$

$$CO + ZnO \rightarrow Zn + CO_2 \qquad [2]$$

$$2Zn + O_2 \rightarrow 2ZnO \qquad [3]$$

Powdered coal is introduced into the slag bath with a deficiency of air for complete combustion. Reaction 1 takes place within the bubbles and the zone of reduction is confined to the immediate boundaries of these bubbles, indicated by reaction 2. At this point metallic zinc is released as a vapor that rises rapidly to emerge from the slag and become reoxidized as quickly as the necessary oxygen is available according to reaction 3. The net thermal effect of these reactions is obviously equivalent to the complete oxidation of the reducing agent.

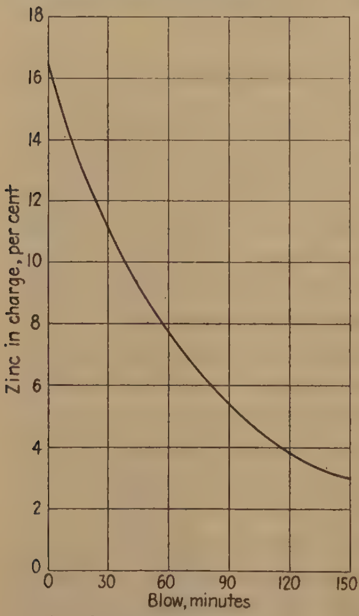


FIG. 7.—ELIMINATION RATE CURVE, FEBRUARY, 1936.

Lead, with its high vapor tension either as the metal or oxide, is volatilized quickly at the temperature of the slag.

The ideal curve in Fig. 7 shows the rate of zinc elimination. During the latter part of the blow the lead content of the fume drops so that it would be quite feasible to separate the product into high-lead and low-lead fume if desirable. In fact, such a separation actually takes places to some extent, regardless of its desirability. The fume grows progressively leaner in lead as the baghouse is approached, where it assays 10 per cent Pb as compared to 20 per cent directly behind the boiler.

Since the slag is constantly being splashed about in the highly reducing atmosphere above the charge, it is probable that some reduction takes place there as well as below the surface of the charge.

Because of the large discrepancy between the theoretical and practical amounts of reducing agent required, it has been urged that furnace design might have an important bearing on this point. As the coal-air bubbles are released close to the vertical side walls, the movement of the slag is up the side wall, across and down at the center line of the furnace. The inference, based on the assumption that the major reducing reactions take place on the bubble boundaries, is that an increase in the area of these boundaries would result in more rapid reduction. This might be accomplished by reversing the motion of the slag, so that a continuous stream of small bubbles would be swept away from the tuyere pipes towards the center of the furnace, where they would be joined by similar streams from the opposite side and be swept to the surface on the center line of the furnace. However, such speculations would necessarily have to be tested in an experimental furnace.

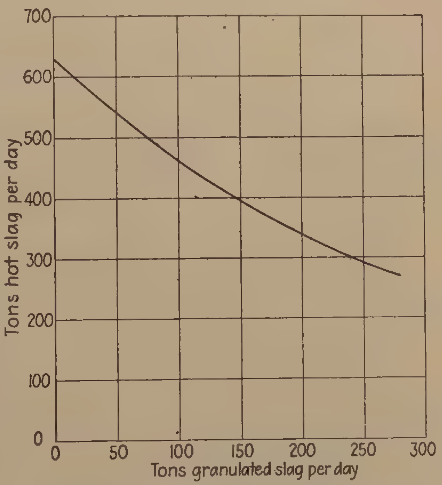


FIG. 8.—CAPACITY OF FUMING FURNACE IN TREATING MIXED CHARGE OF HOT AND COLD SLAG.

At Trail, all the preliminary work was carried out on hot slag only. When it appeared that sufficient hot slag was not available to keep the furnace running at capacity, tests were made on the use of a proportion of cold slag added to the hot charge. It was found that reduction of a charge made up partly of cold slag was rather slower than with an all-hot charge, and further, that granulated slag slowed the reduction less than either crushed or broken pot shell. In consequence, it is cheaper to smelt pot shell in the blast furnaces and use granulated slag to make up any deficiency in hot slag charge.

It has been noted above that 2½ tons of granulated slag will replace 6½ tons of hot slag on the charge. This figure is derived from the weights of a car of slag and a pot and is rather conservative. The ratio of cold slag to hot slag increases as the amount of hot slag in the charge decreases (Fig. 8).

After the plant had been in operation for some time it was evident that the rate of reduction varied periodically above and below normal. Subnormal periods definitely coincided with the addition of dry dross to the blast-furnace charge. Following this clue further, it was shown that a small increase in the sulphur content was responsible for a proportionate increase in zinc in the re-treated slag.

Tests on bituminous and subbituminous coals indicate that, so far as reduction is concerned, there is no difference in either fuel consumption or operation with either coal, provided the ash content is the same.

OPERATING DATA

The average analysis of the hot slag charged to the fuming furnace in 1935 was: Pb, 3.6 per cent; Zn, 16.3; Cu, 0.21; SiO_2, 19.3; Fe, 30.6; Mn, 0.64; CaO, 7.4; Al_2O_3, 5.1; MgO, 1.3; S, 2.0.

Analysis of fuming-plant products is given in Table 1.

TABLE 1.—*Fuming-plant Products at Trail in the Year* 1935

Products	Analysis, Per Cent											
	Pb	Zn	Cu	S	Sulphate S	SiO_2	Fe	Mn	CaO	Cd	As	Sb
Baghouse fume	9.6	67.7	0.06	0.9	0.8	0.4	0.2	0.05	0.2	0.07	0.09	0.09
Flue dust	16.6	57.2	0.09	1.4	1.2	2.2	0.8	0.06	0.3	0.07	0.17	0.09
Boiler cleanings	16.6	44.4	0.19	0.7	0.5	9.1	5.7	0.15	1.7	0.04	0.10	0.09
Clinker	9.0	24.8	0.29	0.5		21.0	14.1		4.1			

Total charge: 183,426 tons, made up as follows: hot slag, 168,725 tons (92 per cent); granulated slag, 12,871 tons (7 per cent); crushed flue slag (clinker), 1,440 tons (0.8 per cent); holding-furnace flux, 390 tons (0.2 per cent).

The fuel used was a mixture of bituminous coals carrying about 21 per cent volatile and a subbituminous coal of 37 per cent volatile. The mixture averaged about 22 per cent volatile matter while fixed carbon and ash were 60.4 and 17.6 per cent respectively.

Coal consumption was 46,439 tons, or 25.3 per cent of the charge, which, had the charge consisted of hot slag entirely, would have been 23.6 per cent.

Waste-heat steam production amounted to 241,879 tons, or 6.66 lb. of steam from and at 212° F. per pound of coal.

Metal production was 26,068 tons of zinc and 6,360 tons of lead in fume, which corresponds to recoveries of 88 per cent of the zinc and 96 per cent of the lead. Silver recovery was 62.4 per cent. The slag after treatment assayed 3.4 per cent Zn and 0.03 per cent Pb.

Excluding two weeks when the plant was shut down for construction work, the fuming furnace operated for 95 per cent of the time. The largest part of the lost time, 10 days, was occupied in digging and repairing flues. Boiler overhaul and furnace maintenance each amounted to four days. Outside trouble, that is, when no slag was available, accounted for three days. Of course during a shutdown maintenance work is going on throughout the plant and the figures quoted are prorated among the various units.

APPENDIX

The Electrolytic Zinc Plant of the Consolidated Mining and Smelting Company of Canada, Limited

(Pages 540 to 572)

PUMPS

The materials used for pump construction vary according to the nature of the solution handled. The pump materials in use are the result of extended experiment and are all giving satisfactory results. Research is still in progress, particularly with stainless steel and rubber lining, both of which show considerable promise. Following are the materials used:

For tank-room acid, carrying about 100 grams per liter free sulphuric acid, hard lead is used. Stainless steel is under investigation. Duriron is satisfactory, but requires very careful handling to prevent mechanical breakage.

For pulps containing low acid (10 grams per liter), abrasive solids, ferric iron, copper, etc. pumps are made of hard lead. Stainless steel is satisfactory.

For pulps containing no acid but carrying abrasive materials and copper, bronze is used.

Pulps containing acid (10 grams per liter), copper, iron and nonabrasive solids require lead pumps. Rubber linings are under investigation.

Clear neutral solutions containing copper are handled in bronze pumps; neutral solutions free of copper, acid, abrasive material, etc., in iron or bronze.

The hard lead used contains 13 per cent antimony. The stainless steel has the following analysis: Cr, 20.0 per cent; Ni, 7.0; C, 0.25; W, 4.0; Cu, 2.0.

INDEX

(NOTE: In this index the names of authors of papers and discussions and of men referred to are printed in SMALL CAPITALS, and the title of papers in *italics.*)

A

- Aguas Calientes: unusual volatilization of lead, odd experience, 28
- AHRENTS, A.: pioneer in blast-furnace lead smelting, 18, 21
- Amarillo silicon carbide retorts, manufacture, 441
- American Blower Co., 397
- American Cyanamid Co.: improvements in Trollhättan electrothermic zinc process, 577
- American Metal Co., Ltd., 410
- American Smelting and Refining Co.: chlorine dezincing in lead refining, 264
  - Cottrell plants, 332
  - debismuthizing lead, 205
  - Federal plant, lead smelting, 106
  - silicon carbide retorts, 441
  - treating lead blast-furnace drosses at East Helena, 160
- American Zinc and Chemical Co., Langeloth, Pa.: typical zinc-roaster log, 400
  - zinc roasters, 387
- Anaconda Copper Mining Co.: electrolytic zinc, 454, 463
- ARGALL, P., 353, 357
- Arsenic: recovery: lead blast-furnace smelting: Midvale, Utah, 53
- ASHCROFT, E. A., 353, 453
- Australia: electrolytic zinc plants, 463
  - Port Pirie: continuous lead refining, 226
- Australian mechanical feeder, 30
- Avonmouth, horizontal retort practice of zinc smelting of National Smelting Company, Ltd., 418

B

- BACH, H., HÄNIG, W., GEHRHARDT, W., THEURICH, E. AND LANGNER, W.: *Magdeburg Zinc Works of Georg von Giesche's Erben Mining Co.*, 465
- Baelen, Belgium: electrolytic zinc plant, 461
  - treatment of residues in ash-fusion gas producer, 698
- Baghouses: automatic: for lead-furnace fumes, 299
  - filtering gases from lead-zinc ores, Midvale, Utah, 51
  - lead smelting: brief history, 26
    - neutralization of gases, 51
  - Jones invention of muslin bag, 343
- Bartlesville: first sintering of zinc ores, 374
- BARTLETT, F. L., 369
- BASSETT, W. H., 359
- Belgian furnace, 618
- Belgium: electrolytic zinc plants, 461
- Bethanizing, 372
- Bethlehem Foundry and Machine Co., roasters for zinc ore, 390
- Bethlehem Steel Co.: electrogalvanized wire, 464
- Bethlehem-Wedge roaster, 391
- BETTERTON, J. O.: *Chlorine Dezincing in Lead Refining*, 264
- BETTERTON, J. O. AND LEBEDEFF, Y. E.: *Debismuthizing Lead with Alkaline Earth Metals, including Magnesium, and with Antimony*, 205
- Betts process. *See* Lead Refining.
- Bismuth: recovery from lead refining, Trail, B.C., 281
- Blast-furnace fumes: lead: baghouse filtering: fires at Midvale, Utah, 52
  - baghouse filtering, Midvale Utah, 51
- Blast-furnace slags: lead: at Trail, 71
  - composition, 101
  - fuming at Trail for recovery of lead and zinc, 67, 721
  - treatment in ash-fusion gas producer, 693, 698
- Blast furnaces: lead: bosh adopted, 18, 22
  - bosh, function, 22
  - crucible shell without heavy reinforcing, 67
  - early types, 20
  - evolution, 20
  - hydrocycle, 21
  - Piltz type, 21
  - rectangular adopted, 21
  - Rachette adopted, 21
  - siphon tap, 18, 21
  - tuyeres, number and size, effect, 64
  - water jacket adopted, 21
  - water jacket important addition, 21
- BLAYLOCK, S. G., 358, 454
- Boilers: zinc redistillation, 447
- Boston & Colorado Smelting Co.: review of operations, Argo plant, 13
- Bradford. *See* Carmichael.
- BRIGHTON, T. B., DICE, C. M. AND OLDRIGHT, G. L.: *Drosses in Lead Smelting*, 127
- Briquetting: zinc ore for vertical retort process, 430

Broken Hill Associated Smelters Proprietary Ltd., continuous lead refining, 226
  Cottrell process at Port Pirie, 331
Bruderlin, E. J.: *Manufacture of Silicon Carbide Retorts*, 441
Brueckner: pioneer in blast-furnace lead smelting, 19
Brunner, Mond & Co., 353, 453
Buck, L. J.: *Lead Smelting in the Federal Improved Mechanical Ore Hearth*, 106
Bunce, E. H. and Handwerk, E. C.: *New Jersey Zinc Company Vertical Retort Process*, 427
Bunce, E. H. and Haslam, H. M.: *Direct-process Zinc Oxide*, 678
Bunker Hill and Sullivan Mining Co.: Cottrell plant, 322
  U. S. Bureau of Mines examination of fundamentals of operating units, 82
Bunker Hill smelter: blast-furnace practice, 73
Butts, A.: *Discussions: on Electrolytic Solder*, 296
    on Trollhättan Electrothermic Zinc Process, 596

C

Cadmium: production in sintering of zinc ores, 384
  recovery: by electrolysis: residues from zinc leaching, 478, 481, 538, 564
    from redistillation of zinc, 445
    lead smelting: Midvale, Utah, 53
      Trail, 72
California Zinc Co.: sintering zinc ores with sintering machine only roasting device, 377
Canada: electrolytic zinc plants, 457
Carmichael-Bradford sintering process: lead ores: brief history, 38
Casting zinc. *See* Zinc Casting.
Cerro de Pasco Copper Corporation: Betts process at Oroya, lead refining, 283
Champion, J., 339
Charcoal: lead smelting: early use, 24
Chisholm, O. P.: *Treating Blast-furnace Drosses*, 160
  Discussion on A Study of Drosses from Lead Blast Furnaces, 192
Cia. Minera de Peñoles, Mapimi, Dgo., Mexico: separation of speiss in lead smelting, 125
Clevenger: G. H.: *Blast-furnace Practice at Midvale, Utah*, 45
Cockerill, A. B., 354
Coke: lead smelting: early use, 24
    modern use, 24
    at Trail, 72
Colorado Smelters' Clearing House, 15
Condensers: zinc smelting: summary of qualities required, 623
Consolidated Mining and Smelting Company of Canada Ltd.: Cottrell process, 323
  electrolytic lead refinery: Betts process, 271
  electrolytic zinc plant, Trail, B. C., 454, 455, 540
Consolidated Mining and Smelting Company of Canada Ltd.: fuming lead blast-furnace slag for recovery of lead and zinc, 721
  lead blast-furnace practice, 59
  silver refinery, 281
  U. S. Bureau of Mines examination of fundamentals, 82
Convers, G. G., 354
Conveying: zinc plants: summary of present practice, 615
Copper-arsenic system: equilibrium relations, 149
Copper-iron-lead-sulphur system: equilibrium relations, 145
Copper-lead-arsenic system: equilibrium relations, 148
Copper smelting: early custom smelting, U. S. A., 13
Cornelius process for treating blue powder, 367
Corstorphan plug cock, zinc leaching, 505
Cottrell process: brief history, 26
  cadmium and lead precipitation from sintering zinc ores, 386
  development, 306
  at electrolytic zinc plant, 323
  on gases from Dwight-Lloyd sintering machines, 325
  gold and silver refineries, 336
  lead and zinc fumes: brief bibliography, 337
  at lead and zinc plants, 72, 304, 546
  precipitators: types, 314
  sulphuric acid mist collection, 306, 328
  at Waelz process plants, 335
  zinc roasting: suspension process, 546
  zinc sulphide furnaces at Trail, 327
Cowper-Coles, S. O., 454
Crutcher, E. R. and Woolf, W. G.: *Electrolytic Zinc Plant of the Sullivan Mining Company*, 527

D

Daggett, E.: pioneer in blast-furnace lead smelting, 19
Dagner condenser, 350
Debismuthizing lead. *See* Lead Refining.
Deitz, L. S.: *Discussion on Electrolytic Solder*, 296
De Laval, G.: electric zinc smelting, 366, 573, 597
Dengg, K.: *Discussion on Electrolytic Solder*, 297, 298
Dice, C. M., Oldright, G. L. and Brighton, T. B.: *Drosses in Lead Smelters*, 127
Dillinger, B., 340
Direct process for manufacture of zinc oxide. *See* Zinc Smelting.
Distillation (*See also* Zinc Smelting): governing conditions, 445
Doerner, H. A.: *Reduction of Zinc Ores by Natural Gas*, 636
Dony, D., 341
Dor-Delattre furnace, 351, 355, 618
Dor press, 347, 350
Drossing. *See* Lead Refining; Lead Smelting.
Duralloy: rabbles for zinc roasters, 396
Dust and fume collection (*see also* Baghouses, Cottrell, Zinc Smelting, etc.):
  lead smelting: growth, 25

Dust and fume collection: zinc plants: summary of present practice, 614
  zinc roasters: Sirocco, 397, 407
  zinc roasting, suspension process, 546
Dwight, A. S.: *A Brief History of Blast-furnace Lead Smelting in America*, 9
Dwight-Lloyd process (*see also* Sintering):
  lead ores: brief history, 35, 38
  diminishes lead poisoning of workers, 36
  double roasting; introduction, 36

E

Eagle-Picher Mining & Smelting Co.: automatic baghouses for lead-furnace fumes, 299
  lead smelting in ore hearth, 117
Edgar, S. C., 354
Eilers, A.: pioneer in blast-furnace lead smelting, 18, 22
Electrogalvanizing: development, 464
Electrolytic cadmium. *See* Cadmium.
Electrolytic zinc: aluminum cathodes: sticking and corrosion, 561
  chemical control of plant, 554
  current efficiency: effect of acidity and temperature, 517
  early process, 352, 453
  development of processes, 453
  electrogalvanized wire, 464
  high-density, high-acid process, 527
  impurities in solution, harmless, detrimental or beneficial, 553
  increase in use of process: causes, 361
  intermediate between high and low acid in system, 465
  low-acid system, 540
  Magdeburg plant, Germany, 465, 474
  plants, completed or under construction, 455 et seq.
  process more advantageous than electrothermic smelting, 594
  Prodorite tanks, 558
  production: tons, compared with retort, 455
  production: world, 455
  purity, 464
  residues: treatment in ash-fusion gas producers, 693
  Risdon, Tasmania: plant, 511
    production, 482
  Sullivan Mining Co., 527
  Tainton process, 463, 527
  Trail, B. C.: plant of Cons. Min. & Smelt. Co. of Canada, 540
  world survey, 453
Electrolytic Zinc Company of Australasia, Ltd.: Cottrell process at Risdon, Tasmania, 330
  electrolytic zinc plant at Risdon, Tasmania, 482
Electrostatic separation: Huff process: lead ores, 48
Electrothermic zinc process. *See* Zinc Smelting.
Englehard, V., 454
Eureka, Nev., cradle of lead blast-furnace smelting, 11
Evans-Wallower Zinc Co.: electrolytic zinc, 464

F

Feddersen, P. C. and Lee, H. E.: *Blast-furnace Practice at the Bunker Hill Smelter*, 73
Federal improved mechanical ore hearth, lead smelting, 106
Fires in baghouse section: Midvale, Utah: lead-zinc ores, 52
Fisher, K. E. and Ravitz, S. F.: *Equilibrium in Lead Smelting*, 118
Flash roasting: zinc ore: introduction, 364
  Trail, B. C., 541
Flin Flon. *See* Hudson Bay Mining and Smelting Co.
Flotation: lead-zinc ores: Midvale, Utah, 50
  role in zinc metallurgy, 361
  zinc: granular residues from leach, 495
Flotation concentrates: zinc: pelleting, 378
  sintering, 378
Fume: definition, 304
Fume and dust collection. *See* Dust.
Fuming lead blast-furnace slag, Trail, B. C., for recovery of lead and zinc, 721
France: electrolytic zinc plants, 461
Fulton, C. H.: *Discussion on Trollhättan Electrothermic Zinc Process*, 594
Furnaces: Angleur: early, 347
  Belgian design, 341, 342
  Birkengang: early, 347
  Dor-Delattre, 351, 355, 618
  drossing, lead smelting. *See* Reverberatory (below)
  Eichhorn-Liebig 350
  fuming: for recovery of lead and zinc from lead blast-furnace slag, 722, 725
  Gerstenhöfer: early, 349
  Hasenclever, 350
  Hauzeur: early, 347
  Loiseau: early, 347
  Muensterbusch: early, 347
  regulus, 57
  retort: horizontal: Avonmouth, England, 418
  retorts. *See* Retorts.
  reverberatory: drossing, lead smelting: construction features, 162
    development, 160
    softening, lead bullion, 199
  Rhenania, 350
  Rhenish design, 342
  rotary, for rolling metallic powder produced in condensers, Trollhättan, 574, 587
  Siemens, early, 345
  Stolberg, 341
  traveling-grate, 685, 690
  van Gluck, 618
  Welzer, 351
  Wetherill, 679
  zinc distillation: summary of characteristics, 616
  zinc-roasting: early, 349
    modified Leggo at Risdon, 485
  zinc smelting: summary of characteristics, 339 et seq.

G

Galvanizers' dross: treatment, 372
Galvanizing. See Electrogalvanizing.

Gas producer: ash-fusion: treatment of lead-furnace slags, 693, 698
    treatment of residues from electrolysis of zinc, 693
    treatment of tin-bearing residues from lead furnace, 693, 699
    Viviez apparatus, 693
Gaskill, E. C.: inventor of an electrothermic zinc process, 599
Gehrhardt, W., Bach, H., Hänig, W., Theurich, E. and Langner, W.: *Magdeburg Zinc Works of Georg von Giesche's Erben Mining Co.*, 465
Gepp, H. W., 358
Germany: electrolytic zinc plants, 461
Giesche Spólka Akcyjna: electrolytic zinc, 461
Gold refineries: Cottrell precipitators, 336
Greene, G. U.: *A Study of Drosses from Lead Blast Furnaces*, 171; *discussion*, 193
Gyles, T. B.: *Horizontal Retort Practice of the National Smelting Company, Limited, Avonmouth, England*, 418

H

Hahn, O. H.: pioneer in blast-furnace lead smelting, 18
Hall, A. E.: *Softening of Lead Bullion*, 194
Hall, R. G., 369
Hallows, R. L. and O'Harra, B. M.: *Modern Automatic Baghouses for Collection of Lead-furnace Fumes*, 299
    Discussion on Lead Smelting in Improved Ore Hearth, 117
Handwerk, E. C. and Bunce, E. H.: *New Jersey Zinc Company Vertical Retort Process*, 427
Hänig, W., Bach, H., Gehrhardt, W., Theurich, E. and Langner, W.: *Magdeburg Zinc Works of Georg von Giesche's Erben Mining Co.*, 465
Hanley, H. R.: *Discussions: on Electrolytic Solder*, 295
        on Equilibrium in Lead Smelting, 125
Hannay, W. H., Stimmel, B. A. and McBean, K. D.: *Electrolytic Zinc Plant of the Consolidated Mining and Smelting Company of Canada, Limited*, 540
Harper, T. E. Jr. and Reinberg, G.: *Betts Process at Oroya, Peru, S. A.*, 283
Harris, W. E.: *The Waelz Process*, 702
Haslam, H. M. and Bunce, E. H.: *Direct-process Zinc Oxide*, 678
Hauzeur furnaces, 617
Health of workers: lead smelting: danger of lead poisoning lessened by Dwight-Lloyd process, 36
        Missouri, 81
        precautions at Avonmouth smelter, 425
    zinc leaching: precautions, 479
Hearth. *See* Ore Hearth.
Heberlein, C. A.: *Discussion on Equilibrium in Lead Smelting*, 125
Heberlein, M.: *Discussion on Electrolytic Solder*, 295 et seq.
Heberlein process. *See* Huntington.
Heberlein, M. and Hermsdorf, R P. E.: *Electrolytic Solder*, 289
Hecksher, A., 353
Hegeler, E. C.: early work, 343
    furnaces, 346, 350, 356, 617
Herculaneum: lead smelting. *See* Lead Smelting: Missouri.
Hermsdorf, R. P. E. and Heberlein, M.: *Electrolytic Solder*, 289
Hixon, H.: experience with unusual volatilization of lead, 28
Hobson and Sylvester, 340
Hoepfner, C.: work on electrolytic zinc, 353, 453
Hudson Bay Mining and Smelting Co., Ltd., electrolytic zinc plant at Flin Flon, Manitoba, 457
Huff process: electrostatic separation: lead ores, Midvale, Utah, 48
Huntington-Heberlein process, brief history, 33, 38
Hydrocycle, 21

I

Ingalls roasting process. *See* Warner-Ingalls.
Ingalls, W. R.: *History of the Metallurgy of Zinc*, 339
    Intermittent Zinc Distilling from Ore, 610
International Smelting and Refining Co., Tooele, Utah: U. S. Bureau of Mines examination of fundamentals, 82
Iron-copper-sulphur system: equilibrium relations, 147
Italy: electrolytic zinc plants, 461

J

Japan: electrolytic zinc plants, 462
Jones, D. B. and T. D., 367
Jones, S. T.: inventor of muslin bag for collection of zinc fume, 344
Jorgensen, E. L.: *Discussions: on Equilibrium in Lead Smelting*, 124
        on Trollhättan Electrothermic Zinc Process, 595

K

Karsten, 340
Kern, E. F.: *Discussion on Electrolytic Solder*, 296, 298
Kilns: zinc smelting. *See* Waelz process.
Kleeman condenser, 350
Krejci, M. W.: *Discussion on Electrolytic Solder*, 297
Krom, S. R., 353

L

Laist, F., 358, 454
Landis, W. S.: *The Trollhättan Electrothermic Zinc Process*, 573; *discussion*, 594 et seq.
Langner, W., Bach, H., Hänig, W., Gehrhardt, W. and Theurich, E.: *Magdeburg Zinc Works of Georg von Giesche's Erben Mining Co.*, 465

Lanyon, R., 354
Laszczynski, S., 454
Lathe, F. E.: *Discussion on Equilibrium in Lead Smelting*, 123
Lead: recovery by fuming lead blast-furnace slag, 721
Lead-antimony system: equilibrium relations, 179
Lead-arsenic system: equilibrium relations, 176
Lead-copper-antimony system: equilibrium relations, 178
Lead-copper-arsenic system: equilibrium relations, 174
Lead-copper-sulphur system: equilibrium relations, 139
Lead-iron-antimony system: equilibrium relations, 178
Lead-iron-arsenic system: equilibrium relations, 172
Lead-nickel-antimony system: equilibrium relations, 179
Lead-nickel-arsenic system: equilibrium relations, 176
Lead ores: flotation. *See* Flotation.
  milling: electrostatic separation by Huff process: Midvale, Utah, 48
Lead refineries: continuous process: Port Pirie, South Australia, 250
  desilverizing, North America, 17
  electrolytic: Betts process: Trail, B. C., 271
Lead refining: Betts process: refinery. *See* Lead Refineries.
  bismuth recovery, Trail, B. C., 281
  continuous: advantages, 247
    costs, Port Pirie, South Australia, 249
    dezincing, 229, 241, 259
    Port Pirie, South Australia, 226
    zinc recovery, 229
  cupellation, Port Pirie, South Australia, 244, 261
  debismuthizing: Betts process: limitations, 205
    Pattinson process: limitations, 205
    with magnesium, 205
    with alkaline earth metals, 205
    with antimony, 205
    with calcium, 205
  desilverizing: continuous, Port Pirie, South Australia, 239, 255
  dezincing: Betterton machine, 265
    with chlorine, 264
    use of product to make marketable zinc chloride, 268
  dross-furnace products: gold distribution: laboratory fusion experiments, 120
    silver distribution: laboratory fusion experiments, 120
  drossing: continuous, Port Pirie, South Australia, 226, 230, 252
  electrolytic: Betts process: Oroya, Peru: acid loss and dip washing, 285
    Betts process: Oroya, Peru: anode corrosion, 284
      difference from usual Betts process, 283
      pilot plant, 287
      standard practice, 286
Lead refining: electrolytic: Betts process: Trail, B. C., 271
    parting: Port Pirie, South Australia, 245, 262
  gold and silver removal by Parkes process not economic if copper content of bullion is large, 229
  impurities should not reach refinery in large quantities, 203
  Missouri, 81
  parting: Port Pirie, 245, 262
  silver refining, Trail, B. C., 281
  silver-gold recovery, Port Pirie, 232, 243
  silver-zinc retorting: Port Pirie, South Australia, 243, 260
  softening: alkali salts, basic principle of use, 201
    continuous: Port Pirie, South Australia, 226, 234, 251
    elimination of antimony, arsenic and tin, 196, 198
    elimination of copper, 196, 197
    furnace. *See* Furnaces.
    problems, 194
    removal of hardening elements, 194
  zinc refining: continuous, Port Pirie, South Australia, 229, 241, 259
Lead smelters: Missouri lead, capacity, 16
  silver-lead plants, North America, 16
Lead smelting:
  blast-furnace: America: brief bibliography, 37
    America, brief history, 9
    arsenic, early removal desirable, 157
    arsenic recovery, Midvale, Utah, 53
    blast, evolution, 25
    Bunker Hill, 73
    cadmium recovery. *See* Cadmium.
    capacity of furnace: U. S. Bureau of Mines experimental work, 82, 103
    charging net residue from zinc oxide leaching plant and filtered discharge of Cottrell humidifying flues, 63
    chemistry, 93
    column: length, effect, 64
    column: low, 75
    copper, early removal desirable, 157
    custom ores: Midvale, Utah, 45
    dross disposal by circulating back through furnace, 54
    dross furnaces. *See* Furnaces.
    drosses: analysis, 127
      composition, 127, 136
      microscopic examination, 131
      study of, 171
      treatment, 127, 160
    drossing: dispering agents, 193
      operation, 168
      in reverberatory, advantages, 69
        amount of scrap iron desirable, 180, 191, 192
        flowsheet changes suggested, 151
        treatment, 160
      effect of precious metals, 156
      at Trail, 68
    early metallurgists, 9, 18

Lead smelting: blast-furnace: equilibrium: laboratory fusion experiments, 118, 124
  experimental work on fundamentals of operating units, U. S. Bureau of Mines, 82
  feed composition: U. S. Bureau of Mines experimental work, 83
  feeding: mechanical: growth, 28
    hood above feed floor with inclined gas offtake at center of top, 61
    thimble, advantages and disadvantages, 61
  furnace construction. *See* Blast Furnaces.
  gases, top: analyses, 99
  gold and silver recovery: difficulties, 122
  hearths. *See* Ore Hearth.
  Huntington-Heberlein process: brief history, 33
  loading: U. S. Bureau of Mines experimental work, 103
  matte: composition, 136
    microscopic examination, 131
    treatment, 129
  Midvale, Utah, 45
  Missouri, 77
  mush in furnace, 68
  operation at forced capacity, 73
  partial softening: objectives, 128
  plants, early, U. S., 12
  preparation of ore: brief history, 33
  products, 118
  separator used for disposal of speiss, 125
  silver and gold recovery: difficulties, 122
  sinter: condition when it reaches furnace, 59
  sintering. *See* Sintering.
  slag (*See also* Blast-furnace Slag):
    as guides in operation: brief history, 30
  softening: partial, objectives, 128
  speiss: composition, 136, 189
    disposal by separator, 125
    from reverberatory drossing furnace: study of, 171
    microscopic examination, 131
  splitting charge, 63
  sulphur, early removal desirable, 157
  Trail practice, 59
  unusual volatilization of lead, Hixon's experience, 28
  wet charge, 63
  zinc recovery: at Trail, 70
 Colorado Smelters' Clearing House, 15
 drosses: brief bibliography, 158
 dust and fume collection. *See* Dust Collection.
 Dwight-Lloyd process. *See* Dwight-Lloyd.
 fuels: early days to 1936, 24
 impurities should be removed before bullion is produced, 203
 lead: reduction: factors controlling, 23
 muscular metallurgy, 19, 20
 ore hearth. *See* Ore Hearth.
 ore-hearth practice: concentrates amenable, 106
   Federal improved, 106
   fuel, 107, 117
   Galena, 117
   process, 109
   salient features, 107
 poisoning of workmen. *See* Health.
 roast reduction process, 106
 sintering. *See* Sintering.
 slags. *See* Blast-furnace Slags.
 tin-bearing residues: treatment in ash-fusion gas producer, 693, 699
Lead sulphate: sintering for blast-furnace feed, 42
Lead-zinc ores: milling: recovery of zinc, Midvale, Utah, 48
Lebedeff, Y. E. and Betterton, J. O.: *Debismuthizing Lead with Alkaline Earth Metals, including Magnesium, and with Antimony*, 205
Lee, H. E. and Feddersen, P. C.: *Blast-furnace Practice at the Bunker Hill Smelter*, 73
Lehigh Zinc Co., 343
Létrange, L.: early work on electrolytic zinc, 352, 453
Linville, C. P.: *Discussions: on Equilibrium in Lead Smelting*, 122
  on Trollhättan Electrothermic Zinc Process, 597
Lithopone, manufacture, history, 372

M

Mac Michael improvement of ore hearth, 112
Magdeburg zinc works, Georg von Giesche's Erben Mining Co., 465
Mansfeld works, Germany: Waelz process, 712
Matthiessen, F. W., 343
McBean, K. D., Stimmel, B. A. and Hannay, W. H.: *Electrolytic Zinc Plant of the Consolidated Mining and Smelting Company of Canada, Limited*, 540
McIntyre, P. F.: *Electrolytic Lead Refinery, Betts Process, the Consolidated Mining and Smelting Company of Canada Limited*, 271
McNaughton, R. R.: *Slag Treatment for the Recovery of Lead and Zinc at Trail, British Columbia*, 721
Meister, H. C., 354
Melting zinc. *See* Zinc Melting.
Methane: reduction of zinc ores. *See* Zinc Smelting.
Midvale: lead blast-furnace practice, 45
  zinc recovery in milling, 48
Miller, V. and Oldright, G. L.: *Smelting in the Lead Blast Furnace*, 82
Missouri: lead blast-furnace smelting, 77
Morse, P. S.: mechanical feeder, 30
Mount Isa Mines, Ltd., Cottrell process at lead and zinc smelter, 328
Murray, G. E.: *Lead Blast-furnace Practice at Trail, B. C.*, 59
Muscular metallurgy, 19, 20

N

Nahnsen, G., 352
National Smelting Co., Avonmouth, Wales: sintering zinc ores as feed for retort furnaces, 378
National Zinc Co.: first sintering of zinc ores, 374
Natural gas: reduction of zinc ores, 636
Neill, J. W.: pioneer lead metallurgist, 34
Neureuther, C. F., 357
New Jersey Zinc Co.: direct process for manufacture of pigment zinc oxide, 678
  refining zinc by redistillation, 445
  vertical retort process, 365, 427
Newnam ore hearth: operation, 111
Norske Zinkkompani, 460, 701
Northport Smelting & Refining Co., Cottrell plant, 320
Norway: electrolytic zinc plants, 460

O

O'Harra, B. M. and Hallows, R. L.: *Modern Automatic Baghouses for Collection of Lead-furnace Fumes*, 299
  Discussion on Lead Smelting in Improved Ore Hearth, 117
Oldright, G. L.: *Discussion on A Study of Drosses from Lead Blast Furnaces*, 190
Oldright, G. L., Dice, C. M. and Brighton, T. B.: *Drosses in Lead Smelters*, 127
Oldright, G. L. and Miller, V.: *Smelting in the Lead Blast Furnace*, 82
Ore hearth: development, chronological, 111
  Federal improved: construction, 112
    operation, 114
  MacMichael patents, 112
  modern: construction, 107
  Newnam, operation, 111
  Scotch: construction, and use, 77, 106, 111
  smelting in. *See* Lead Smelting.

P

Passaic Zinc Works, 344
Pecos ore: roasting. *See* Zinc Roasting.
Peirce, W. M. and Waring, R. K.: *New Jersey Zinc Company Process for the Refining of Zinc by Redistillation*, 445
Pelleting: zinc flotation concentrates, 378
Phillips, A. J.: *Discussion on Trollhättan Electrothermic Zinc Process*, 595
Poland: electrolytic zinc plants, 460
Porter, J. A.: pioneer lead smelter, 21
Prodorite tanks, electrolytic zinc process, 558
Producers: gas. *See* Gas Producers.

R

Raht, A.: pioneer in blast-furnace lead smelting, 19
Ravitz, S. F.: *Discussion on Equilibrium in Lead Smelting*, 123 et seq.
Ravitz, S. F. and Fisher, K. E.: *Equilibrium in Lead Smelting*, 118
Reinberg, G. and Harper, T. E. Jr.: *Betts Process at Oroya, Peru, S. A.*, 283
Retorts: lead refining: 36-cwt. capacity, 243
  zinc smelting: horizontal: composition, 419
      dimensional limits, 419
      quality required, 420
    silicon carbide: manufacture, 441
    summary of qualities required, 620
    vertical: size, 428
Rhenish furnaces, 618
Rhodesia: electrolytic zinc plants, 462
Riddell, G. C.: improved technique of Dwight-Lloyd process: double roasting, 36
Rigg, G., 362
Risdon. *See* Electrolytic Zinc.
Rissmann, O., 355, 363, 374
Roasters: zinc flotation concentrates: Pecos ore: Bethlehem Foundry and Machine Co., 390
      Warner-Ingalls improvements, 387
    cooling-air circulation reverse of normal, 389, 391
    dust collection on Bethlehem-Wedge roaster, 397, 407
    rabble corrosion: prevention, 396
    screw feeders, 391
Roasting: zinc ore. *See* Zinc Roasting.
Roitzheim-Remy retorts, 365
Rowand, L. G., 353
Ruhberg, J., 340
Russia. *See* Union of Soviet Socialist Republics.

S

St. Joseph Lead Co.: electrothermic zinc-smelting process, 599
  sintering zinc ores with sintering machine only roasting device, 377
  vertical retort process, 365
Savelsberg sintering process: lead ores: brief history, 38
Scotch hearth. *See* Ore Hearth.
Selby Smelting & Lead Co.: review of operations, 13
Shower roasting. *See* Flash Roasting.
Siemens furnaces, 617
Siemens-Halske, 454
Silver: recovery: in lead refining, 239, 243, 250, 255, 281
    in zinc leaching, 503
Silver refineries: Cottrell precipitators, 336
  Trail, B. C., 281
Singmaster, J. A., 368
Sintering (*see also* Dwight-Lloyd):
  fume collection by Cottrell process, 325
  lead ores: brief history, 38
    Carmichael-Bradford process: brief history, 38
    double roasting: brief history, 40
    Dwight-Lloyd process: brief history, 35, 38
      double roasting, 36
    Huntington-Heberlein process: brief history, 38
    mixing and preparation of charge, 43

- Sintering: lead ores: possibility of using SO_2 for making acid, 44
    - Savelsberg process: brief history, 38
  - lead sulphate: for blast-furnace feed, 42
  - lead-zinc ores: double: advantage, 78
    - long vs. short machines, 91
    - metallic lead production, 92
    - Missouri, 77
    - moisture in charge: effect, 89
    - prerequisites to improvement, 92
    - recirculation of gases: effect, 91
    - thin vs. thick beds, 92
    - U. S. Bureau of Mines experimental work, 87
  - zinc flotation concentrates, 378
  - zinc ores: action of sulphate, 379
    - cadmium production, 384
    - carbon as fuel, 376
    - Cottrell apparatus for catching lead and cadmium fume, 386
    - early methods at Bartlesville, 374
    - feed for retort furnaces, 378
    - five times: feed for electric furnaces, 377
    - formation of "concrete," 380
    - high in iron, 375
    - introduction, 362
    - preroasted: for manufacture of sulphuric acid, 381
    - procedure most likely to be satisfactory in U. S., 383
    - production of SO_2 for manufacture of sulphuric acid, 378, 381
    - Rigg process, 362.
    - St. Joseph Lead Co., 606
    - salt addition to charge, effect, 386
    - sintering machine only roasting device, 377
    - sulphide, Avonmouth, England, 421
    - summary of present practice, 612
    - vs. shelf roasting: costs, relative, 382
- Sirocco: dust collection on zinc-ore roasters, 397, 407
- Slaskie Kopalnie i Cynkownie, Spólka Akcyjna, electrolytic zinc, 461
- Smith, W. C., 367
- Snow, W. C.: *Electrolytic Zinc at Risdon, Tasmania*, 482
- Société Française des Métaux et Alliages Blancs: treatment of tin-bearing residues in ash-fusion producer, 699
- Société de la Vieille-Montagne: beginning, 342
  - electrolytic zinc, 461
  - treatment of residues in ash-fusion gas producer, 693
- Softening lead bullion. *See* Lead Refining.
- Solder: lead-tin: electrolytic: analysis, 295
      - copper removal, 297
      - process, 289
    - older methods of producing, 289
- Spelter: derivation of term, 339
- Spólka Akcyjna, electrolytic zinc, 461
- Sprague, C. B.: neutralization of gases from lead-zinc ores before filtration through baghouse, 51
- Stehli, H. J.: *Sintering Lead Ores*, 38
  - *Sintering Zinc Ores*, 374
- Stimmel, B. A., Hannay, W. H. and McBean, K. D.: *Electrolytic Zinc Plant of the Consolidated Mining and Smelting Company of Canada, Limited*, 540
- Stöger, W., 454
- Stone, G. C., 354
- Sullivan Mining Co.: electrolytic zinc plant, Kellogg, Idaho, 463, 527
- Sulphuric acid: manufacture at Magdeburg zinc plant, 470
  - manufacture from zinc blende: beginning, 350
    - history, 371
  - mist: collection by Cottrell process, 306, 328
  - possibility of manufacture from SO_2 from sintering lead ores, 44
  - sintering zinc ores for production of SO_2, 381
- Sylvester and Hobson, 340
- Swartz, C. E.: *Discussions: on A Study of Drosses from the Lead Blast Furnace*, 193
  - *on Electrolytic Solder*, 297
- Sweden: Trollhättan electrothermic zinc process, 573
- Swinburne, J., 454

T

- Tainton electrolytic zinc process, 527
- Tasmania: electrolytic zinc plant, 463, 482
- Theurich, E., Bach, H., Hänig, W., Gehrhardt, W. and Langner, W.: *Magdeburg Zinc Works of Georg von Giesche's Erben Mining Co.*, 465
- Tin refining: electrolytic: purity of product, 298
- Trail, B. C. *See* Consolidated Mining and Smelting Company of Canada, Ltd.
- Trollhättan electrothermic zinc process: copper recovery, 589
  - early practice, 573
  - gold recovery, 589
  - improvements by American Cyanamid Co., 577
  - lead recovery, 589
  - power consumption, 586, 591, 594
  - the process, 366, 573
  - record of two campaigns, 585
  - silver recovery: by liquation, 589
  - silver recovery: from zinc-iron alloy, 590
  - zinc recovery, 589

U

- Union of Soviet Socialist Republics: electrolytic zinc plants, 460
- United States: electrolytic zinc plants, 463
- U. S. Bureau of Mines: development of reduction of zinc ores by natural gas, 636
  - lead smelting in blast furnace: experimental work, 82
  - study of drosses in lead smelters, 127
- U. S. Metals Refining Co.: electrolytic solder, 289
- U. S. Smelting, Refining & Mining Co.: lead blast-furnace practice at Midvale, Utah, 45
- Utah Engineering Experiment Station, University of Utah: experiments on equilibrium in lead smelting, 118
  - study of drosses in lead smelters, 127

Utah: Midvale: lead blast-furnace practice, U. S. Smelt., Ref. & Min. Co., 45

V

Van Oirbeek, J.: *Treatment of Residues from Electrolysis of Zinc and of Lead-furnace Slags in Ash-fusion Gas Producers*, 693
Vieille Montagne. *See* Société.
Viviez, France: electrolytic zinc plant, 461
  treatment of residues in ash-fusion gas producer, 693
von Giesche's Erben, G.: electrolytic zinc, 461
  first furnace, 340
  Magdeburg zinc works, 465
Von Liebnau: pioneer in blast-furnace lead smelting, 19

W

Wabner, R., 345
Waelz process: apparatus, 703
  introduction, 369
  kilns in operation, 719, 720
  Mansfeld works, Germany, 712
  operation, 702
  plants: Cottrell collection, 335
  ring formation: removal, 711
Waring, R. K. and Peirce, W. M.: *New Jersey Zinc Company Process for the Refining of Zinc by Redistillation*, 445
Warner, C. M.: *Lead Blast-furnace Practice in Missouri*, 77
Warner, M. F.: *The Warner-Ingalls Zinc-roasting Process*, 387
Wartenweiler, A.: pioneer in blast-furnace lead smelting, 19
Water jacket. *See* Blast Furnaces.
Weaton, G. F.: *St. Joseph Lead Company's Electrothermic Zinc-smelting Process*, 599
Welch, H. V.: *Collection of Lead Zinc Dusts and Fumes by the Cottrell Process*, 304
Welzer, G., 355, 617
Wetherill furnace: eastern type, 367, 679
  western type, 367, 683
Wetherill, J. P., 346, 353
Wetherill, S.: zinc-smelting process, 343, 368, 679
Wharton, J., 343
Wilfley, A. R., 353
Williams system of mechanical feeding, 29
Williams, G. K.: *Continuous Lead Refining at Port Pirie, South Australia*, 226
Woolf, W. G. and Crutcher, E. R.: *Electrolytic Zinc Plant of the Sullivan Mining Company*, 527

Z

Zentner, A.: *World Survey of Electrolytic Zinc*, 453
  Discussions: on A Study of Drosses from Lead Blast Furnaces, 190
    on Trollhättan Electrothermic Zinc Process, 594
Zimmer, B. N., 410

Zinc: for cartridge brass: cadmium not detrimental, 359
  electrolytic. *See* Electrolytic Zinc.
  recovery by fuming lead blast-furnace slag, 721
  recovery at Midvale, Utah, 48
  world production in 1860, 345
    in 1880, 348
Zinc casting: Risdon, Tasmania, 519
  Sullivan Mining Co., 537
  Trail, B. C., 572
Zinc chloride: marketable: made from product of chlorine dezincing in lead refining, 268
Zinc distillation. *See* Zinc Smelting.
Zinc flotation concentrates: cadmium content, Trail, B. C., 564
Zinc leaching:
  arsine poisoning. *See* Health.
  batch, single-stage, 491
  batch system, 531
  cadmium recovery, 478, 538, 564, 581
  cobalt precipitation, 359, 496, 534
  Corstorphan plug cock, 505
  Magdeburg, Germany, 471, 473
  purification: Risdon, Tasmania, 496
    Trail, B. C., 551, 569
  residues: production of work lead, Magdeburg plant, 481
  Risdon, Tasmania, 491
  Sullivan Mining Co., 530
  Trail, B. C., 545, 547, 567
  silver recovery, 503
Zinc melting: cathode zinc: Magdeburg, Germany, 477
    Risdon, Tasmania, 519
    Sullivan Mining Co., 537
    Trail, B. C., 571
Zinc metallurgy: role of selective flotation, 361
  technical practice of last 75 years, history, 339
Zinc ores: reduction by natural gas. *See* Zinc Smelting.
  sintering (*see also* Sintering): vs. shelf roasting: costs, relative, 382
  various: analyses, 583
Zinc oxide: pigment: direct process of manufacture, 678
Zinc refining: adjunct to lead desilverizing. *See* Lead Refining.
  product of horizontal retorts, Avonmouth, England, 425
  redistillation: boiler construction, 447
    New Jersey Zinc Co., 445
    recovery of other metals, 452
  summary of practice, 370
  Trollhättan, 590
Zinc roasting: air introduction by cold-air fans, 469
  autogenous: early practice, 387
  blende for sulphuric acid, beginning, 350
  burning concentrate process, 541
  dust collection. *See* Dust.
  flash: introduction, 364
    Trail, B. C., 541
  flotation concentrates: Magdeburg plant, Germany, 468
    Pecos ore: Warner-Ingalls process, 387
      costs in 1933, 416

- Zinc roasting: Risdon, Tasmania, 482
  - roasters. *See* Roasters.
  - shower: introduction, 364
    - Trail, B. C., 541
  - Sullivan Mining Co., 530
  - sulphuric acid manufacture: Magdeburg, 470
  - summary of present practice, 611
  - suspension process: introduction, 364
    - Trail, B. C., 541
    - vs. sintering: costs, relative, 382
  - two-stage, Risdon, Tasmania, 482
  - Warner-Ingalls process, 399
    - operating results on Pecos ore, 403, 405, 410
    - sampling, 414
    - typical log, 400
- Zinc smelting: American process of producing pigment zinc oxide, 678
  - blast-furnace: Trail, B. C., 59
  - continuous: introduction and growth of process, 364
    - vertical retort, 427
  - difficulties, inherent, 427
  - direct process: history, 367
    - manufacture of pigment zinc oxide, 678
  - distillation. *See* retort (below).
  - electrothermic: history, 573
    - less advantageous than electrolytic process, 366, 594
    - ore-preparation difficulties, 577
    - prevention of explosions in condensers, 578, 587
    - St. Joseph Lead Co.: plant control, 599, 609
    - trials in Montana, 594
    - Trollhättan process. *See* Trollhättan.
  - French process of producing pigment zinc oxide, 678
  - fume and dust collection. *See* Cottrell.
  - galvanizing dross: reduction by natural gas, 662
  - Hegeler process, 346, 350, 356, 617
  - indirect process of producing pigment zinc oxide, 678
- Zinc smelting: in kilns. *See* Waelz process.
  - oxide, pigment: American process of producing, 678
    - direct process of manufacture, 678
    - French process of producing, 678
    - indirect method of producing, 678
    - wet process of producing, 678
  - reduction by natural gas: brief bibliography, 677
    - combination of concurrent travel of ore and gas in first part of reaction zone followed by countercurrent travel of ore and recirculated exit gas in second stage of reaction, 648
    - condenser adapted to process, 649
    - economic possibilities, 673
    - pretreating ore to eliminate impurities, 661
    - preventing reoxidation by catalyzed reactions and maintaining the reactions at maximum efficiency, 640
  - reduction with methane, 354, 636
  - retort: early practice, 341
    - hand vs. mechanical charging, 627
    - horizontal at Avonmouth, England, 418
      - workmen's wages, 424
    - intermittent: labor required, 632
      - summary of present state of art, 610
      - zinc loss, 628
      - zinc recovery, 629
    - refining product. *See* Zinc Refining.
    - vertical: advantages of New Jersey Zinc Company's process, 439
      - commercial application, 440
      - continuous, 427
      - New Jersey Zinc Co., 427
  - volatilization: early attempts, 702
    - Waelz process, 702
  - Waelz process. *See* Waelz Process.
  - wet process of producing pigment zinc oxide, 678
- Zinc sulphate: electrolytic process, Létrange, 352

3 8198 309 333 001
THE UNIVERSITY OF ILLINOIS AT CHICAG

THIS BOOK IS FOR USE
ONLY IN THE LIBRARY
IT DOES NOT CIRCULATE